Meines

Don't Touch

ELEMENTARY CHEMISTRY

n acid is a substance which pro
ces hydrogen ions when dissolved in
ter or other dissociating liquid HCl
base is a substance which prod
s   hydroxy ions when dissolved
water or other dissociating liquid
Salt is a substance produced
the union of the anion of acid
cation of base $\overset{+}{Na}\overset{-}{Cl}$
cation anion

Neutralization is the union of the hyd
ion of acid + hydroxyl ion of base
form water $HCl + NaOH = NaCl +$
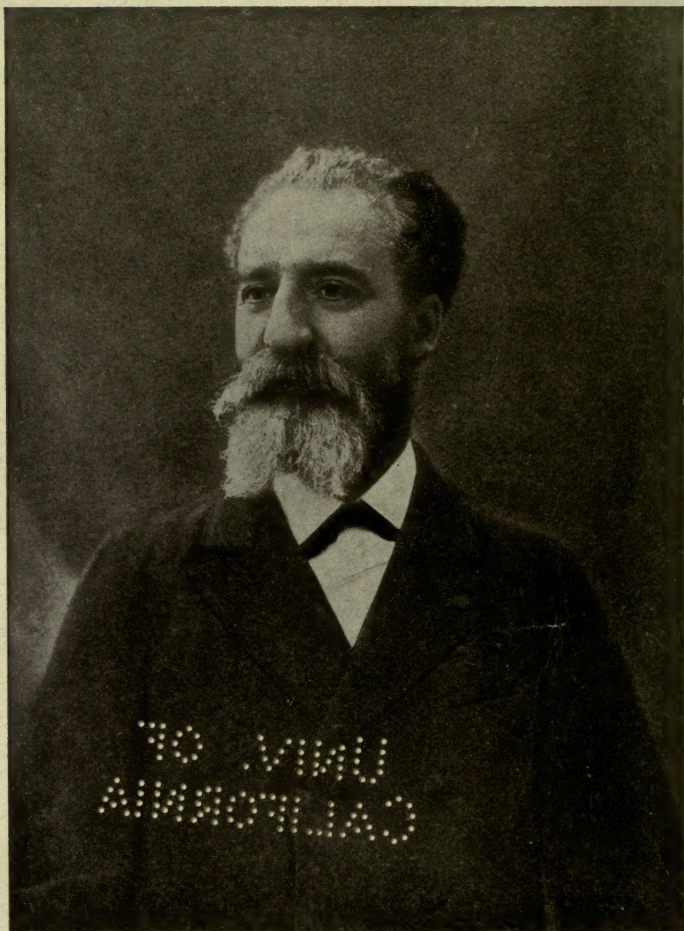
HENRI MOISSAN

B. Paris, Sept. 28, 1852.

ELEMENTARY
CHEMISTRY

BY

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PREFACE

In this book I have attempted to write a brief account of the present state of chemical science for the use of those beginning the subject in colleges and secondary schools. I have tried to make the book represent the subject as it is *to-day*, and I believe that everything that lies within its scope in the later literature has been considered with a view to its admission or exclusion. It is difficult to avoid errors in a work of this kind, and I can hardly hope that I have completely succeeded in doing so, but, at all events, any blunders which the book may contain are my own property, for I have not consciously copied after any existing manual, and I have settled all cases of doubt as to the correctness of a statement by critical consideration of the original memoir.

The book may fairly claim to be regarded as an *independent* account of the subject. It is the outgrowth of about ten years of high-school teaching, and I have been careful to include nothing in it which I have not taken up successfully and repeatedly with ordinary classes. This is the only safe criterion, and I have felt compelled to follow it, though it has resulted in the exclusion of some generalizations which I should have been glad to admit. I believe that in this way I have entirely avoided the danger of becoming unintelligible to the beginner.

pleasure to express here my gratitude for the care with which he has carried out this exacting task.

Prof. Edgar F. Smith, director of the Chemical Laboratory of the University of Pennsylvania, has been good enough to read the manuscript and to favor me with his opinions as to its arrangement and availability as a text-book for beginners.

Dr. E. A. Partridge, of the Central Manual Training School, has read the work both in proof and manuscript and has made a number of valuable suggestions.

The Laboratory Manual aims to supply a serviceable outline of experimental work to accompany the text. The precise directions which are given for the performance of the experiments will, I trust, save the teacher much useless repetition, while the constant precautionary suggestions will somewhat lighten his burden of responsibility. If the directions are properly followed, the experiments can be carried out without danger of any kind.

I believe it to be unwise to place phosphorus in the hands of beginners, and the substance is employed only once in the course. In this instance the danger is slight, but the experiment can be carried out on the lecture-table if preferred.

Almost all the experiments can be performed with very simple and inexpensive materials. Perhaps half a dozen require somewhat expensive apparatus—the Hoff-mann apparatus for electrolysis, a U-shaped endiometer with three-way stop-cock, an induction coil and two burettes are the most important. Some will prefer to carry out these experiments on the lecture-table. However, I have not labeled them " teacher's experiments," since I believe the decision should be left to the teacher himself.

The object of the questions which are scattered through the manual is to afford assistance in the difficult and essential task of making the student do his laboratory work in

a thoughtful spirit. The materials for answering the questions are all contained either in the text or in the laboratory exercises, and they should be answered by the student, not by the teacher, save as a last resort.

In the preparation of the Laboratory Manual free use has been made of the available publications on the subject of experimental chemistry. The recommendations of the College Entrance Examination Board, the Committee of Ten on Secondary School Studies, of the Board of Regents, and of Professor Richards, of Harvard, have been carefully considered and have afforded me much valuable assistance. About thirty of the cuts are after drawings made by my wife, and six from original photographs; the remainder are taken from various sources.
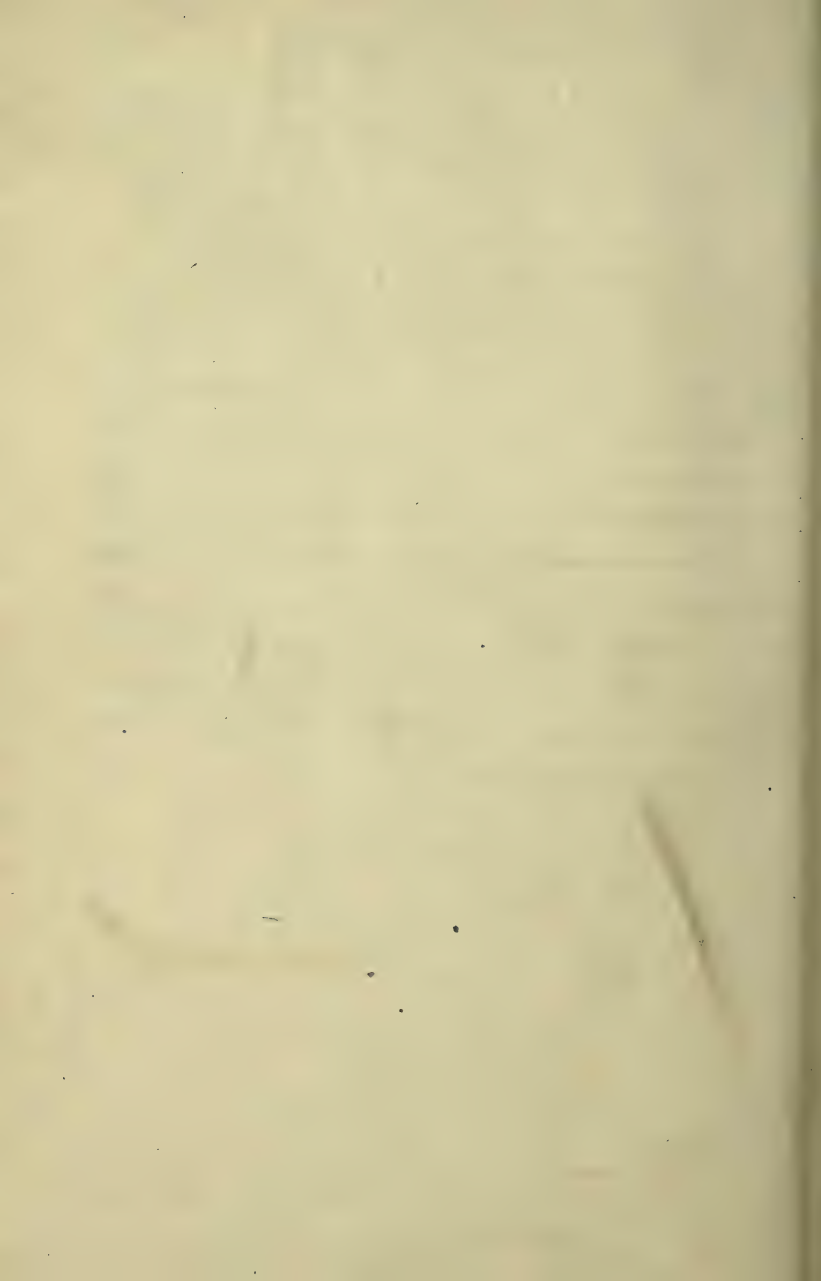
R. H. B.

Central Manual Training School, Philadelphia.

CONTENTS

LIST OF PORTRAITS

xiii

ELEMENTARY CHEMISTRY

CHAPTER I

WATER

1. **EVERY** one is familiar with the bodies called ice, liquid water, and steam. Most people are aware, also, that these three things are not regarded as different substances, but merely as three different forms of the same substance. Now, a clear idea of the meaning of this statement is of the first importance in chemistry as well as in other branches of knowledge. At the outset, therefore, it is desirable to make a careful study of ice, water, and steam, and then to consider what we mean by the statement that they are different forms of the same thing.

2. **Occurrence of water.**—Water is abundant in nature. When an excavation is made to a sufficient depth, water collects in the lower portion. In this way we become aware that everywhere below a certain level—called the water-line —the rocks are saturated with water. Of course the water-line, the upper limit of the water in the rocks, is not a line, but a surface. Its depth varies much in different places, and at the same place in different seasons. Where it rises to the surface of the soil there is a body of water, river, lake, or ocean, according to the conditions, while in deserts and dry regions generally it is met with at some distance below the ground. Many rocks—e. g., granite—contain large

quantities of water in the form of minute drops, enclosed in the crystals which make up their mass.

Some rocks—e. g., serpentine—are *compounds* containing water. In these the presence of the water is not evident on inspection, but becomes plain when the water is liberated in some way. When, for example, a small piece of such a rock is heated in a glass tube sealed at one end, drops of water condense in the cool part of the tube. In this state of *chemical combination* water makes up an important part of the mass of the earth's crust.

The water of nature is never pure. Even rain-water dissolves substances from the atmosphere, that which falls at the beginning of the rain being more impure than the later portions, and, of course, the water that oozes through the rocks takes up from them (dissolves) a great variety of substances. The purest natural water is that which results from the melting of ice.

3. **Preparation of pure water.**—In order to obtain a water pure enough for the purposes of the chemical labora-
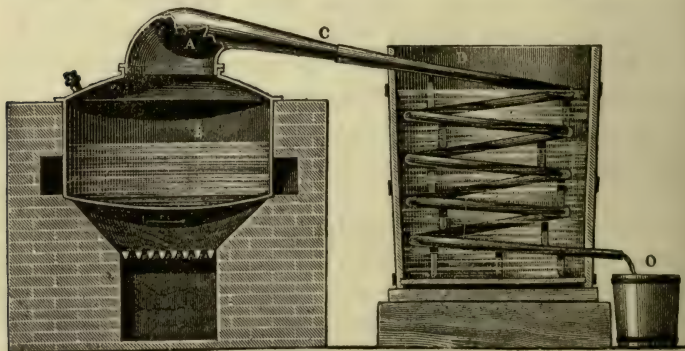
Fig. 1.—Distillation of water.

tory, natural water is converted into steam by being heated in a copper vessel, *B*, and the vapor is passed into a tube of tin or copper, *D*, which is kept cool by water circulating

outside it. Here the steam condenses, the earthy impurities have been left behind in the vessel in which the water was boiled, and the purer water is collected in another vessel, *O*. This process is called distillation, and is frequently applied to the purification of other substances (Fig. 1).

Distilled water contains traces of substances—ammonia and nitrogen, for example—from which it is difficult to free it. For certain special purposes it can be further purified by a process of fractional freezing. The water is partially frozen and the liquid rejected. Then the ice is melted and the partial freezing repeated, and so on for eight or ten operations. In this way water of extraordinary purity can be obtained, but never perfectly pure. In fact, such a thing as an "absolutely pure substance" has never been obtained. All that our methods of purification can do is to reduce the impurities to such small quantities that we are unable to detect them, and they have no effect on the behavior of the substance.

4. **Physical properties.**—Thin layers of water appear transparent and colorless, but in a layer of two meters or over it has a distinct blue color. A beam of light passed into water is just as invisible as in a vacuum or in dust-free air. At all temperatures water or ice gives off into the space in contact with it the vapor of water. If this space is enclosed, if, for example, the water is placed in a dish and covered with a bell-jar, then the water will evaporate at any fixed temperature until every unit of volume of the enclosed space contains a definite quantity of the vapor. The higher the temperature the more water-vapor exists in every cubic centimeter of the space, but at any fixed temperature the quantity is always the same. In other words, the vapor pressure of water in contact with the liquid is always the same at the same temperature, and this pressure increases as the temperature rises. This is the form in which the statement is usually made, and it is true not only of water,

but also of all pure substances, solid or liquid, which evaporate unaltered.

In open vessels the water is diffused into the surrounding air, and no such saturation of the space can occur; hence the water evaporates completely. Heated in open vessels the vapor-pressure of the water rises until at 100° it equals the average pressure of the air, and the liquid boils. When boiling has once begun the total heat supply is consumed in converting the water into steam, and no rise in temperature occurs until the liquid has disappeared. This boiling away at a constant temperature, pressure remaining the same, is common to all pure substances. Mixtures of two substances—e. g., a mixture of alcohol and water—often show a gradual rise in the boiling temperature as the quantity of liquid decreases, but there are many mixtures which boil away at a constant temperature, like a pure substance.

5. Freezing of water.—When water at the ordinary pressure is cooled to 0° it begins to solidify. No fall of temperature takes place during the freezing until all the water has become ice. By proper precautions freezing can be avoided and the liquid cooled to —10° or lower, but as soon as it begins to freeze the temperature rises to 0°, and when ice melts the temperature remains the same until the ice is all melted. It is impossible to heat ice above 0°.

All pure substances behave like water;[1] each melts and solidifies at a constant temperature. However, many mixtures behave in the same way. And all solids which are pure single substances are like ice in this respect, that it is impossible to heat them above their melting-points.

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[1] In this paragraph and the preceding one it is assumed that the substance is heated in open vessels—that is, under the pressure of the atmosphere. In most cases the temperature at which a solid melts is raised when the pressure is increased. Ice is an exception. Its melting temperature is lowered when the pressure is raised.

6. Action of pure water on the system.—Electrical resistance.—The purest water is a poison to micro-organisms, and causes vomiting and other disturbances in the human system. Distilled water is too pure to be wholesome, and certain waters which occur in nature, for instance the water formed by the melting of the ice of the Swiss glaciers, are so pure that they are quite unfit for use.

Water offers an enormous resistance to the passage of the electric current. In passing through a column of water one millimeter in length the current experiences as much resistance as in a copper wire of the same cross-section long enough to encircle the earth at the equator a thousand times.

7. Ice.—Ice, like water, is blue in large masses. It is composed of small imperfect crystals; and, according to the size of these, the properties of the mass vary slightly. Thus, when water has been cooled below the freezing-point and then caused to freeze suddenly by agitation, the ice is whiter, softer, less transparent, and more filled with air-bubbles than ordinary ice. The most obvious difference between ice and liquid water is that ice is a solid, by which we mean that it has a shape of its own which it retains, while water takes the shape of the containing vessel.

Steam in thin layers appears colorless. In large masses it is blue; and the color of the sky is, in part, due to the water-vapor of the air. The white cloud commonly called steam consists of fine drops of water. The density of steam is only a little more than one-half that of the air. This low density is one important distinction between vapors and the liquids from which they are obtained. Under ordinary pressure the vapor is always immensely lighter than the liquid. Another difference is that the liquid left to itself has a limiting upper surface, the vapor has not.

8. Composition and chemical behavior.—There are two important methods of investigating the composition of a

substance. Either it is separated into its constituents, which is *analysis,* or the constituents are brought together and the substance produced. This is called *synthesis.* Both methods can be employed with water. Water can be separated into its components by heat, but the temperature required is extremely high. The most convenient method of analysis is furnished by the electric current.

9. **Electrolysis of water.**— The apparatus (Fig. 2) has a central tube, which serves as a funnel for filling it with liquid; in the two side-tubes collect the gases which are given off during the process. The current, coming from any suitable source, passes into platinum wires which are fused through the glass and end in small pieces of platinum foil, one in each of the side-tubes. These pieces of foil are called the electrodes, and it is there that the products of the decomposition appear. It has been said that the electrical resistance of pure water is enormous. For this reason the apparatus is filled with water, to which there has been added about one-tenth of its volume of sulphuric acid, which greatly increases the conductivity of the liquid. It is impossible to explain the rôle of the sulphuric acid in an elementary work, further than to say that while it conducts the current it is found unaltered after the experiment, and only the water is decomposed. As soon as the current is made to pass, it is seen that bubbles of colorless gas collect, and are evolved from both electrodes. When some gas has collected the stop-cocks at the top may be opened and a burning match applied to the issuing gases. One is com-
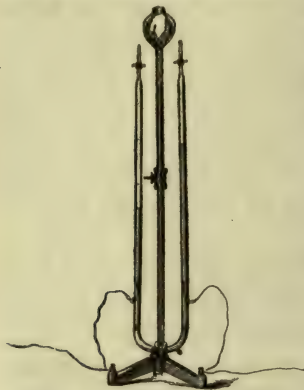
Fig. 2.—Electrolysis of water.

bustible, burning with a pale blue flame; the other is not, but if the flame is extinguished and the match-stick, still bearing a spark, is held in the gas the wood bursts into flame at once. The combustible gas is called *hydrogen*, and the one which supports combustion so much better than air is *oxygen*.

Now the stop-cocks may be closed and the gases allowed to accumulate. It will be seen that twice as much hydrogen collects at the negative electrode as of oxygen at the positive.

Thus, when water is decomposed by the electric current, two volumes of hydrogen and one of oxygen appear.

10. **Synthesis of water.**—The conclusion that water is composed of these two gases in these proportions can be cor-
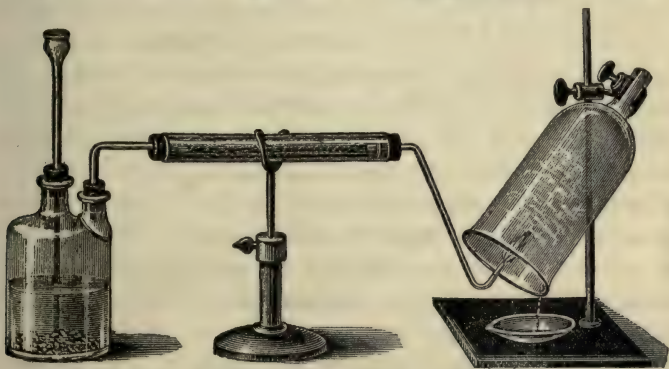
FIG. 3.—Formation of water by burning hydrogen.

roborated by synthesis. That water is a compound of hydrogen and oxygen can be shown in a simple manner by burning a jet of dry hydrogen under a cold jar, when drops of water condense on the glass (Fig. 3). This experiment gives us no information about the quantities in which the gases enter into the compound. Such information is readily obtained by means of the apparatus (Fig. 4). The curved tube is called an *eudiometer*. It is first filled

with mercury, and then a mixture of two volumes of hydrogen and one of oxygen is introduced. A spark from an induction coil is then caused to pass between the two platinum wires in the limb of the tube bearing the stop-cock, the thumb being held tightly over the open end of the tube at the same time. There is an explosion, and the mercury rises and apparently fills the tube completely. Both gases have disappeared, and the steam produced condenses to liquid water, the volume occupied by which is very small by comparison with that of the gases which combine to produce it. By a simple modification of this experiment the volume of the steam produced can also be measured. All that is necessary is to heat the U-shaped tube to a temperature above that at which the steam condenses. This is accomplished by surrounding it with a wider tube and passing, through the space between, the vapor of some liquid which boils at a higher temperature than water. Amyl alcohol is a suitable liquid. The apparatus is represented in Fig. 5. The result shows that the volume of the steam is equal to that of the hydrogen. We have already seen that this is double the volume of the oxygen. Hence, **2 volumes hydrogen + 1 volume oxygen = 2 volumes steam.**
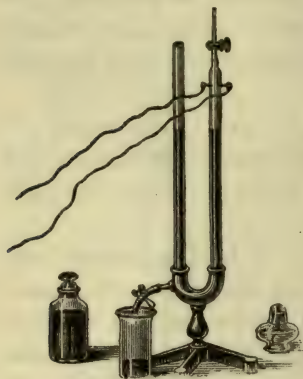
Fig. 4.—Synthesis of water.

Fig. 5.—Synthesis of water. Measurement of volume of the steam.

Thus the relation by volume of

Hydrogen : steam   = 2 : 2 or 1 : 1.
Oxygen : steam   = 1 : 2.
Hydrogen : oxygen = 2 : 1.

It is important to notice how very simple these relations are.

11. **Composition of water by weight.**—When once we know the composition of water by volume it is easy to calculate its composition by weight. The specific gravity of oxygen referred to hydrogen is nearly 16. This means that a quart or a liter of oxygen will weigh 16 times as much as a quart or a liter of hydrogen. Let us suppose that two liters of hydrogen have combined with one liter of oxygen producing, of course, two liters of steam. If we call the weight of one liter of hydrogen 1, then 2 parts of hydrogen by weight have entered the compound. If oxygen is 16 times as heavy, the liter of oxygen will weigh 16. Thus, 2 parts of hydrogen $+$ 16 parts of oxygen disappear, and, since no weight is ever lost or gained in chemical changes, 18 parts of water must be produced. Water, therefore, contains $\frac{2}{18}$ or $\frac{1}{9}$ of its weight of hydrogen and $\frac{8}{9}$ of oxygen.

This calculation from the volumes of the two gases is sufficient, but we may corroborate the result by a method which proceeds purely by weight. Several compounds of copper and oxygen exist, of which the most important is black, and is called cupric oxide. When it is heated in an atmosphere of hydrogen it behaves like many other oxides; the hydrogen removes the oxygen, producing water with it, and copper as metal is left. An oxide is always a compound of oxygen with some other element, and we say that the oxide is *reduced* by the hydrogen. Now, if we have weighed beforehand the vessel containing the cupric oxide, and if we weigh it again after the experiment, it is clear that the loss in weight is oxygen, which has been removed and has

produced water with the hydrogen. If we have arranged matters so that the water produced has all been collected in another weighed vessel, or in a number of vessels, all of which have been weighed together, the increase in weight of this will be the amount of water produced. And, since the water contains only two things, the weight of the hydrogen can be obtained by subtracting that of the oxygen from that of the water. The result of this process confirms that of the other, and informs us that water contains about 8 parts of oxygen to 1 of hydrogen by weight.

This problem of determining the proportions in which hydrogen and oxygen exist in water is an important one in our science, and recently much careful work has been done upon it. It has been found that the figure 8 is too high, and that water contains 7.94 parts of oxygen to 1 of hydrogen. This figure is probably correct to the second decimal place.

It is important to notice that the composition of water is *always the same*. It can be obtained in nature in various ways. We can distil ocean water, or melt ice, or condense moisture from the air by cooling, and we can prepare it artificially from other substances by hundreds of different methods, for water appears more frequently as a product of chemical changes than any other substance. But when, at last, we obtain pure water, it is always found to consist of hydrogen and oxygen in the same proportions.

12. Decomposition of water by heat.—We have seen that at 100° liquid water passes into steam, the pressure being one atmosphere, and that it is impossible to cause the temperature to rise above 100° until all the liquid has disappeared. Of course, when the liquid is all gone, it is possible to heat the steam to any desired degree. It expands like all gases and vapors until, at a yellow heat, it begins to separate into its elements. The decomposition does not become complete: steam, oxygen, and hydrogen are found together in the vessel. If the temperature is raised further, more of the

steam in the vessel is decomposed, and the higher the temperature the less steam and the more hydrogen and oxygen are found in it. At the highest temperatures at which experiments have been made about half of the steam is split up into its constituents, and this is more than 1,000° above the point at which the decomposition begins. No doubt there is some very elevated temperature at which the decomposition becomes complete. This we know, because many similar cases have been investigated in which the temperatures are not so high, and investigation not so difficult.

Finally, why do we consider ice, liquid water, and water-vapor as three forms of the same substance? Chiefly because we can convert any one of the three into any other without adding or subtracting anything except energy. Subtract heat-energy from water and it becomes ice; add energy to it and it becomes steam. In winter the water-vapor of the air yields up its heat-energy to cold window-panes and becomes ice directly, without passing through the liquid stage.

CHAPTER II

SOLUTION

13. **Solubility and insolubility.**—A little coarsely powdered rosin is placed in a beaker, covered with water, and stirred. There is no apparent effect. The water is poured off, and alcohol added instead. On stirring, the rosin disappears, and it is found that every drop of the alcohol contains it. It will be seen that rosin behaves differently with water and with alcohol, and we express this by saying that it is *insoluble* in the water and *soluble* in the alcohol. A liquid which has acted upon a substance soluble in it and has taken it up in this way is called a *solution*; thus we now have an alcoholic solution of rosin.

Alcohol dissolves many solids which are insoluble in water—for instance, many substances of animal and vegetable origin; but water also dissolves many substances insoluble in alcohol—for instance, numerous compounds of the metals, metallic salts, as they are termed.[1] Thus, when cupric sulphate—a compound of copper, sulphur, and oxygen—is stirred up with alcohol it is unaffected, but when treated with water it dissolves, communicating to the liquid a blue color.

14. **Saturated solutions.**—It is worth noting that any cupric salt which dissolves in water will communicate to it

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[1] It must be pointed out that the term insoluble represents a state of things which probably is never really met with. There is good reason to think, for instance, that there is no substance insoluble in water; but the solubility of some is so very small that it can not be detected.

the same color. In the same way all cobalt salts are red in solution, all nickel salts green, and so on. Now let more cupric sulphate be added, little by little, to the solution, stirring each time until the solid has disappeared before adding the next portion. Finally, there comes a time when the liquid refuses to dissolve any more cupric sulphate, and the latter remains unaltered at the bottom. The solution is now *saturated*. Thus a saturated solution is a liquid which has dissolved all of a given solid that it will dissolve at some temperature which is, or ought to be, stated. One can only speak of a solution as being saturated with respect to some particular solid; otherwise the term has no meaning. Our solution, which is saturated with cupric sulphate, is still able to dissolve other substances. And the temperature must be stated, because the solubility of all substances in all liquids is different at different temperatures.

15. **Effect of temperature on the amount dissolved.**—Let us heat the liquid which still contains some undissolved cupric sulphate. The solid dissolves, and if the liquid is heated just short of boiling, it will dissolve about five times as much cupric sulphate as at the ordinary temperature of the room.

If the solution is now allowed to cool, about four-fifths of the cupric sulphate—that is, the excess above what the water can dissolve at the ordinary temperature—will separate in crystals.

This is the usual behavior of solids; their solubility in liquids is almost always increased by heating. There are a few exceptions. The well-known substance gypsum, or plaster of Paris, is more soluble in water at the ordinary temperature than in boiling water. And there are substances whose solubility is not much affected by change of temperature. Thus table-salt is only slightly more soluble in boiling water than in water at the freezing-point.

16. **Supersaturated solutions.**—Sodium sulphate is a white compound of sulphur and oxygen with the metal sodium. Some water is warmed to about blood heat (37°) and sodium sulphate gradually added. The water dissolves about one-half its weight of the solid. The liquid is freed from undissolved material by pouring it through a disk of porous paper placed in a funnel, and is allowed to run into a clean bottle, which is immediately corked, to prevent the access of dust. It will now cool to room temperature, say 20°, without the separation of any of the dissolved substance. But the *saturated* water solution of sodium sulphate at 20° only contains one-fifth of its weight of the solid. Our solution, which contains nearly three times as much, is said to be *supersaturated.*

A supersaturated solution, therefore, contains more of a substance dissolved than the saturated solution at the same temperature. It can only exist in the absence of the solid which tends to separate from it. A crystal of sodium sulphate is thrown into the bottle containing the supersaturated solution. At once the liquid is filled with crystals of sodium sulphate which are wet with the saturated solution of the salt.

Most substances yield supersaturated solutions to some extent, but some do so much more easily than others, and it is found that those substances which produce large, well-formed crystals yield supersaturated solutions more easily than those which crystallize imperfectly.

Solutions of Liquids in Liquids

17. Some water is placed in a stoppered funnel with a stop-cock at the bottom—a so-called separating funnel. To this ether is added, little by little, the funnel being shaken after each addition. The ether disappears, entering into solution in the water. Upon continuing the addition of ether the water becomes saturated with it, and there separates,

above the solution of ether in water, a second layer. It is usual to call this layer " ether," but this is a loose statement. It is a saturated solution of water in ether. The same two layers might have been produced by putting the ether in the funnel and adding water gradually to it, but in this case the second layer would have formed below, since the solution of ether in water is heavier than the other.

A liquid, then, can dissolve another liquid, just as it can dissolve a solid, and just as in the case of the solid the amount dissolved in the saturated solution at a fixed temperature is always the same.[1] But there is a case with liquids which we do not find with solids. Some liquids appear to be able to dissolve each other to any extent. Thus alcohol and water can be mixed in any quantity whatever, and under no circumstances will two layers be produced. It has been said that with solids, heating almost always increases the amount which a given liquid will dissolve. With liquids the exceptions to this are much more numerous.

Solutions of Gases in Liquids

18. Some water is placed in a thin-walled glass—called a beaker—and heated. Long before the water boils bubbles of gas collect on the walls and finally rise to the surface and escape. The water has dissolved gases from the air. These gases are driven out by boiling, and then the water loses its pleasant flavor and acquires the stale insipidity which is familiar in boiled water. It will be seen from this that the solubility of the gases of the air in water is reduced by heating the water. This is true of the solubility of all gases in all liquids. The solubility of the atmospheric gases in water is slight. Thus of nitrogen, which makes

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[1] In both cases the amount dissolved also varies slightly with the pressure on the surface of the liquid. Under ordinary circumstances the pressure, that of the atmosphere, can be considered constant.

up about four-fifths of the air by volume, water dissolves less than one-fiftieth of its bulk at ordinary temperature and pressure. Some gases dissolve very freely. Water at the freezing-point dissolves, for instance, over eleven hundred times its volume of ammonia gas, and this solution constitutes the water of ammonia of commerce. The law that solubility of gases decreases with rising temperature is well illustrated in this case. When the solution is heated to boiling all but the merest trace of ammonia escapes.

19. **Effect of pressure on the solubility of gases.**—It has been seen that, in the case of solids, the quantity dissolved is affected by pressure, but that the effect is slight and can be neglected. With gases, on the other hand, pressure is an important element. When the solubility of a gas in a liquid is slight the quantity dissolved is proportional to the pressure.

By pressure is meant not the total pressure on the surface of the liquid, but that fraction of it which is exerted by the gas under discussion.

Carbon dioxide, a compound of carbon and oxygen, is a gas of which water, at ordinary temperature and the pressure of one atmosphere, dissolves about its own volume. When the pressure is doubled the quantity dissolved is doubled. Soda-water is water into which about three volumes of carbon dioxide have been pumped under a pressure, therefore, of about three atmospheres. When the liquid is exposed to the air the gas escapes slowly with effervescence. The same state of things exists in effervescent fermented liquors, only here the gas, instead of being pumped into the liquid, is produced in the liquid by fermentation in corked bottles, and, since it has no escape, dissolves in the liquid under its own pressure.

20. **Supersaturated solutions of gases.**—Supersaturated solutions are common with gases. An ordinary glass of plain soda-water is an excellent example. As it stands on

the table the air exerts on the upper surface a pressure of 1 atmosphere. But the quantity of carbon dioxide dissolved does not depend upon this total pressure, but only upon that fraction of it which is due to carbon dioxide.

Now, since the quantity of carbon dioxide in the air is very small, the pressure which this gas exerts on the liquid is practically zero. Hence all the gas should escape. But as a matter of fact the escape is extremely slow, and if the glass is clean and the liquid undisturbed, gas is only given off from the surface.

It has been found possible to pump carbon dioxide into a glass of water under a pressure of three atmospheres, and then remove the pressure without any bubbling. Of course in this case the glass was carefully cleaned and the liquid absolutely undisturbed.

Supersaturated solutions of solids crystallize on throwing in a fragment of the substance which tends to separate. Other solids have no effect. This is an interesting difference between solids and gases. A supersaturated solution of a gas forms bubbles

Fig. 6.—Supersaturated solution of a gas.

—gives off the excess—in contact with any gas whatever, preferably with some other gas. Thus, let a perfectly clean glass tube, sealed at one end, be lowered, open end down, into one glass of soda-water. Bubbles ascend from the plane of contact between air and liquid (Fig. 6).

When a piece of charcoal is dropped into the glass energetic effervescence occurs. The action is the same as in the glass tube. Charcoal is porous and full of air, and it acts as a means by which air can be brought into contact with the liquid.

It is easy to remove the air by heating the charcoal red-

hot and holding it under mercury to cool, and then, when dropped into the solution of carbon dioxide, no bubbles are produced.

Solutions in Solids

21. Even when the valve of a bicycle tire is tight and the tire free from punctures, the air escapes slowly and the tire becomes soft. It is often said that the tire is porous; but this is only another way of saying that in some manner the air passes through it, and does not really help us to understand the matter. Probably most people think of the tire as containing openings too small to be seen, through which the air gradually streams.

The air consists, for the most part, of two gases, one of which, oxygen, has already been mentioned. The other is also colorless and odorless, and is called *nitrogen*. Now, when a tire has become soft, by standing, it is found that the gas which it still contains is nearly pure nitrogen. It is the *oxygen* which has escaped most easily. This is not to be explained by the assumption that oxygen passes through small orifices more easily than nitrogen, for, from other experiments, we know that the reverse is true.

How, then, is the behavior of the rubber tire to be explained? By far the simplest statement to make is that the rubber tire has dissolved the oxygen. We have seen that the solubility of a gas is proportional to the pressure of that particular gas against the dissolving substance. Inside the tire the pressure of the oxygen is very much greater than outside. Hence the oxygen continually dissolves at the inner surface and is given off at the outside.

In the same way rubber will dissolve carbon dioxide. Many facts similar to the behavior of the pneumatic tire are known, and they can all be explained in the same simple way. Thus, when hydrogen is passed into a hot platinum tube, it escapes rapidly through the walls of the tube. It will also pass through a thin plate of iron, even in the cold.

22. Solids can also dissolve liquids.—Every apparently dry powder which has been exposed to the air has obtained from it some water. The presence of the water can be proved by heating the powder in a glass tube, when the water condenses in drops in the cool portion, and the quantity can be ascertained by weighing a portion of the powder, heating it gently, and then reweighing. The difference is the weight of the expelled water. In this way we discover that the quantity of the water—called *hygroscopic* water—depends upon the pressure of the water-vapor in the air, and is greater on wet days than on dry ones.

When a cylinder of lead is placed with its lower surface on a disk of gold, gold dissolves in the solid lead and travels upward in the cylinder, very slowly at ordinary temperatures, and more rapidly when heated. In the same way gold will travel into silver and platinum.

From these last cases it will be seen that *solids can dissolve each other.* Glass is an excellent example of a solution, formed at a red heat in the melting-pot, which solidifies without any separation, and is therefore to be called a solid solution. Very old glass is sometimes dim and almost opaque because the constituents have separated in crystals, just as copper sulphate crystallizes from water when the hot saturated solution is cooled.

Solutions in Gases and Vapors

23. Bromine is a heavy reddish-black liquid which gives off, at ordinary temperatures, a suffocating red vapor. When a small quantity of it is placed in a strong glass tube it evaporates until every cubic centimeter of the space in contact with the liquid contains a certain quantity of the vapor. The color of the vapor will serve as a rough measure of this quantity. Now let air be forced into the tube under strong pressure. At once the color of the vapor becomes more intense, and if we have taken a small enough quantity of

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bromine the liquid in the bottom disappears. By forcing in enough air the color may be made six times as strong as before, which means that six times as much bromine has evaporated. There is no reason why this state of things should not be described by saying that the compressed air has dissolved the bromine. Iodine and camphor behave in a similar way when compressed with different gases. Vapors seem to have the same power. Potassium iodide is a white solid compound of a metal, potassium, with iodine. It will not evaporate below a red heat. It is soluble in alcohol, and, when the solution is enclosed in a strong glass tube and heated, the alcohol becomes a vapor, but the solid still remains dissolved, for the contents of the tube remain perfectly transparent, no crystals separating.

24. **Solution common to solids, liquids, and gases.**—The most important result of all this is that there is no reason to assume that liquids are the only bodies which can act as solvents. Solids, liquids, and gases all possess the power, and all of the three can act as dissolved substance. But the physical nature of a liquid is such that solutions in it are far easier to make and to handle, and hence liquid solutions are more important.

SUSPENSION

25. Rosin is insoluble in water but soluble in alcohol. The alcoholic solution is allowed to fall into a large quantity of water in a cylinder. The liquid is filled with a white turbidity of finely divided solid rosin. The rosin, in this condition, settles very slowly, and is said to be *suspended* in the water, and the state of things before it has settled is called a *suspension*. After a rain the rivers are turbid with suspended matter which is washed into them, and which finally settles, leaving the water clear. If the suspended matter is lighter than the rest of the liquid it will go to the top instead of the bottom. Milk consists of

small fat globules suspended in an aqueous liquid, and, when it is allowed to stand, they collect at the surface, producing the cream.

26. **Suspensions in gases.**—Gases hold suspended matter in exactly the same way. The air is the most familiar example of this. It always contains dust, finely divided iron from meteorites, and the bodies of bacteria. A mist consists of fine suspended water globules. Suspended salt crystals are carried by the winds to points hundreds of miles from the coast.

27. **Distinction between solution and suspension.**—It will be seen that a suspension is a *temporary* condition produced by outside action, as, for instance, by shaking up a powdered solid with a liquid. But solution is a process which takes place of itself, and the result is a *permanent* condition, the natural state of the two substances when in contact. Thus, let some cupric sulphate be placed in a tall glass cylinder, and water carefully poured over it so as not to disturb it. Then let the cylinder be closed, to prevent evaporation, and stood away in a place as free from changes of temperature as possible. Since the cupric sulphate lies at the bottom, it is clear that it is heavier than the water. Nevertheless, it gradually diffuses through the water, and if there is enough water present the final result is a uniform mixture of the two. This is permanent. The cupric sulphate will never settle to the bottom as the rosin did in the other case. It is usually said that a suspension differs from a solution in this respect, that the solid substance can be removed by filtering from the first, but not from the second. Now, it is true that ordinary suspended matter can be removed by filtering, while dissolved matter never can. But any filter, whether of stone or paper, is simply a substance full of small holes which allow the liquid to pass and retain the solid. Plainly, the behavior of any suspension toward a filter depends upon whether the holes in the filter are

smaller than the suspended particles, or the reverse. If smaller, the matter will be removed and the liquid will be clear. If larger, it will pass through. It is easy to imagine and easy to obtain a suspension so fine that it will pass without change through any filter which can be made at present. Thus gold, silver, platinum, and other metals have recently been obtained in exceedingly fine suspension in water. The liquids are dark in color and appear perfectly clear, and the solid particles are so small that they are not visible under the most powerful microscope. But they are suspensions, as is shown by the fact that the metal separates, after a time, as well as by optical methods which can not be discussed here.

CHAPTER III

PHYSICAL AND CHEMICAL CHANGE

THE LAW OF THE INDESTRUCTIBILITY OF MATTER

28. **Changes in matter.**—The material bodies which surround us are subject to continual change. Water left in free air disappears and enters the atmosphere as an invisible vapor, from which it appears again as solid—snow or hail, or as liquid—rain, mist, or cloud, according to the conditions. When cooled it solidifies as ice and acquires quite different properties. Iron left exposed to air and water passes, first at the surface, and at last completely, into a soft, yellowish-red substance quite different from the iron, which we know under the name of *rust*. Bright surfaces of metals tarnish with a speed which depends upon the nature of the metal and of the air with which it is in contact. Even the rocks, so often referred to as examples of permanence, crumble under the influence of the weather into earth or clay, which is finally carried down into the sea and made into rock again. More rapid changes, like those which take place in a coal fire, or in a burning candle, are familiar. Finally, the very complicated changes which take place in the living body must be mentioned.

29. **Physical and chemical change.**—It is convenient to divide changes of the kind referred to into two classes, the nature of which will be clear from a few examples.

PHYSICAL CHANGES

30. **Sulphur.**—A roll of sulphur is brought near to a small ball of pith or cork which hangs by a thread. There is

no result. Now let the roll be rubbed with a cloth, and again brought near the ball. This time the ball is attracted and swings far out of the natural position. By friction the sulphur received an electric charge and this conferred upon it new properties, but it is still sulphur. In a little while the charge is lost and the new properties disappear.

31. **Mercuric iodide.**—Mercuric iodide is a bright-red, heavy powder composed of small crystals. It is a chemical compound of the familiar liquid metal mercury—used in filling thermometers—with iodine, a grayish-black substance looking like graphite. Some mercuric iodide is placed in a tube and gently heated. Slightly above the boiling-point of water a striking change of color to bright yellow occurs, and it can be shown that the shape of the small crystals, of which the powder consists, has changed. After having compared the yellow with the red modification—the two have exactly the same composition, both containing 200 parts of mercury and 254 parts of iodine—the yellow powder is divided into two portions. Half of it is placed on paper and rubbed briskly with a glass rod. At once it changes back again to the red modification. The other half is preserved in a clean tube and, after some time, examined. The same change has occurred: the yellow powder is now red. Evidently the only result of the pressure of the glass rod was to accelerate a change which would have occurred without it if sufficient time was given.

At ordinary temperatures the natural state into which mercuric iodide passes if left to itself is the red modification; at slightly higher temperatures, accurately above 129°, the yellow modification is the natural state, and the red passes into it. We express this by saying that below 129° the red modification is stable, above, the yellow. There is much in all this which reminds us of the change of ice into water and back. Ice and liquid water, like yellow and red mercuric iodide, are two modifications of the same substance.

Below 0° ice is the stable modification; above 0° water. The most important difference is that, in the case of water, one modification is liquid and the other solid, while in the case of mercuric iodide they are both solid.

32. **Tin.**—The properties of all material bodies depend upon the circumstances under which they exist. The most important of these are pressure and temperature, and it is only because pressure and temperature do not vary widely in ordinary life that we are in the habit of regarding the properties of bodies as tolerably constant. In order to fix our ideas, let us think of a cube of tin. It is clear, first of all, that the volume of the cube depends upon the pressure and temperature. With rising temperature it will expand, with increasing pressure it will contract. Whether it is a solid, a liquid, or a vapor is chiefly a matter of temperature. Slight heating easily converts it into a metallic, mercury-like liquid, and, on intense heating, this can be transformed into a vapor. On exposing the cube to winter's cold for a long time, it falls to a loose, dull-gray mass, which is simply another solid modification of tin, and is reconverted into the familiar white lustrous metal at once on heating—for instance, by pouring hot water over it. The vapor, the liquid, and the two solids are all tin; no new substance has been produced.

Changes like the variation in the electrical state of sulphur, the transformation of water into ice, the change of the red mercuric iodide into the yellow and back, the production of the different modifications of tin, all agree in this respect, that no new substance is formed anywhere in the process. Taken together they are called *physical changes,* and their study is the subject-matter of the science of physics.

Chemical Changes

33. **Mercuric oxide.**—This compound of oxygen and mercury is a dense red substance. A little of it is placed in

a hard glass retort,[1] *A*, and heated. The retort is connected with a tube called the delivery tube. This leads away any gas which may be evolved to a vessel where it can be collected in an inverted cylinder full of water, *D* (Fig. 7). The first effect of the heat is to turn the mercuric oxide from red to black. On heating to a higher tempera-
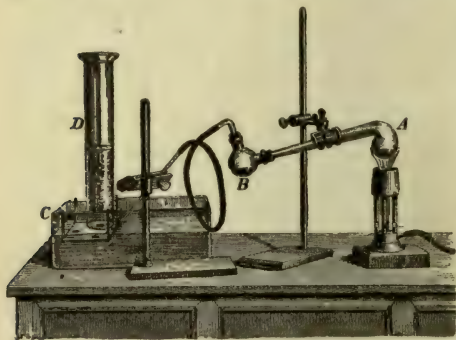

FIG. 7.—Decomposition of mercuric oxide by heat. *A*, retort in which the substance is heated; *B*, receiver in which the mercury collects; *D* and *C*, apparatus for collecting the oxygen over water.

ture, bubbles of a colorless gas rise through the water and fill the inverted cylinder, and if enough mercuric oxide has been taken, several cylinders full of the gas may be collected in this way. Upon investigation the gas proves to be odorless as well as colorless; when a match-stick bearing a spark is placed in a tube full of it, the wood bursts into flame. Remembering the experiment in which we split up water by the electric current, we perceive that this gas is oxygen.

Upon examining the retort it is found that the red powder has disappeared and the retort contains a metallic, mirror-like ring around the upper cool portion and a drop of metallic liquid, both of which are easily seen to consist of *mercury*. The heat has separated the mercuric oxide into its constituents, and almost all compounds behave similarly at a sufficiently high temperature. Here, then, one

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[1] Hard glass is a variety which will stand great heat without melting and is used when the temperature required is high.

substance, mercuric oxide, has disappeared, and two new substances, oxygen and mercury, have arisen in its place. Neither can be regarded in any sense as a form or modification of mercuric oxide. This is a change of a different character from the change of ice to water or of red mercuric iodide to yellow.

34. **Magnesium.**—As another example, let us burn a piece of magnesium ribbon. There is an intense evolution of light and heat, and the result is a white powder of magnesia—*magnesium oxide*—which would weigh, if all collected, considerably more than the magnesium burned. The oxygen of the air has combined with the magnesium and has produced the new substance, magnesium oxide. The change is *chemical*. A *chemical change,* then, is a change in which new substances appear. The study of chemical changes is the province of *chemistry*. For a long time it was held that the task of the chemist was finished when the products of the change had been investigated completely. This view is now given up. The investigation of the products of chemical changes is an important part of chemical science, and it is the part with which this book is chiefly concerned, but it is only a part; after this there follows the study of the change itself, its speed, and the variations in this speed when temperature, pressure, and other conditions alter, and only when this has been accomplished can we claim really to understand the matter.[1]

THE LAW OF THE INDESTRUCTIBILITY OF MATTER

35. Imagine two glass globes which have been sealed tightly, so that nothing can leave and nothing enter them.

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[1] It will be an excellent exercise for the student to classify changes in material things which occur in daily life into chemical and physical. Thus it is easily seen that the various transformations of water and the melting of metals are physical phenomena, while the rusting of iron, the decay of wood, and the burning of a candle are chemical.

Imagine also that the globes contain some material in which a chemical or physical change can occur. As an example of the first we may consider that the first globe is filled with air and contains a piece of magnesium wire. As an example of the second let us consider that the second globe contains some red mercuric iodide. The globe containing the magnesium wire is placed on one side of a delicate scale and accurately balanced by weights placed on the other side. The globe containing the mercuric iodide is treated in the same way.

Now let us cause the two changes to occur. It will be easy to focus the rays of the sun with a lens on the magnesium until it takes fire and burns. The red mercuric iodide can be warmed by the careful application of a flame to the outside of the glass, until it changes to the yellow modification. The globes must now be allowed to cool, for it is impossible to weigh a hot object accurately, owing to air currents. Then they are replaced, each in its own scale. It will be found that the weight of both is unaltered. We might try any number of changes in this way, and the result would always be the same. It is, in fact, impossible to change the weight of the globes except by piercing the glass and taking something out or putting something in through the orifice.

Now the weight measures the quantity of matter in the globes just as the shopkeeper's weights measure the quantities of various substances he hands to his customers. Hence chemical and physical changes produce no alteration in the quantity of matter present. This fact, that nothing is ever gained or lost in any processes which man has investigated, is usually called the *law of the indestructibility of matter*. It is often stated in this form: " The quantity of matter in the universe is constant." But the universe is a large place, and it is dangerous to make statements about what may happen in inaccessible portions of it. There is,

however, no reason why we should not extend the law to our own solar system. On the sun, physical processes and—in the cooler portions of its atmosphere—chemical processes also, take place on a gigantic scale. But any considerable alteration in the mass of the sun would alter the pull which it exerts on the planets, and produce a modification in their motions which the modern telescope could not fail to detect. That no such change is detected shows that the mass of the sun remains the same. Of course the same reasoning applies to the planets and their satellites.

The fact that the length of the year remains the same shows that matter does not appear out of nothing nor vanish into nothing on either the sun or the earth. The fact that the time of an eclipse can be accurately predicted centuries in advance is a very sharp proof that the weights of the sun, the moon, and the earth remain the same.

36. **Importance and nature of the law.**—This law is the foundation of chemical and physical science. Like all the other laws of science, it is simply a descriptive statement which sums up, in a brief way, the result of man's experience. It does not depend at all upon any ideas we may entertain regarding the structure of material things, and is equally true whether we consider them as made up of particles with spaces between them or not. On the contrary, the ideas which we hold upon such subjects must be made to agree with this and other facts, to be presently discussed. Otherwise they are worthless and misleading.

37. **Apparent exceptions.**—Cases which *apparently* contradict this law are common. The disappearance of water exposed to the air and the burning away of a candle without residue are examples. The water is diffused through the air as an invisible vapor. As for the candle, it consists essentially of hydrogen and carbon. When it burns, both combine with the oxygen of the air, the hydrogen to water-

vapor, and the carbon to the colorless gas, carbon dioxide, already referred to. And, of course, the sum of the weights of the candle burned and the oxygen taken from the air must be equal to the sum of the weights of the products of the burning.
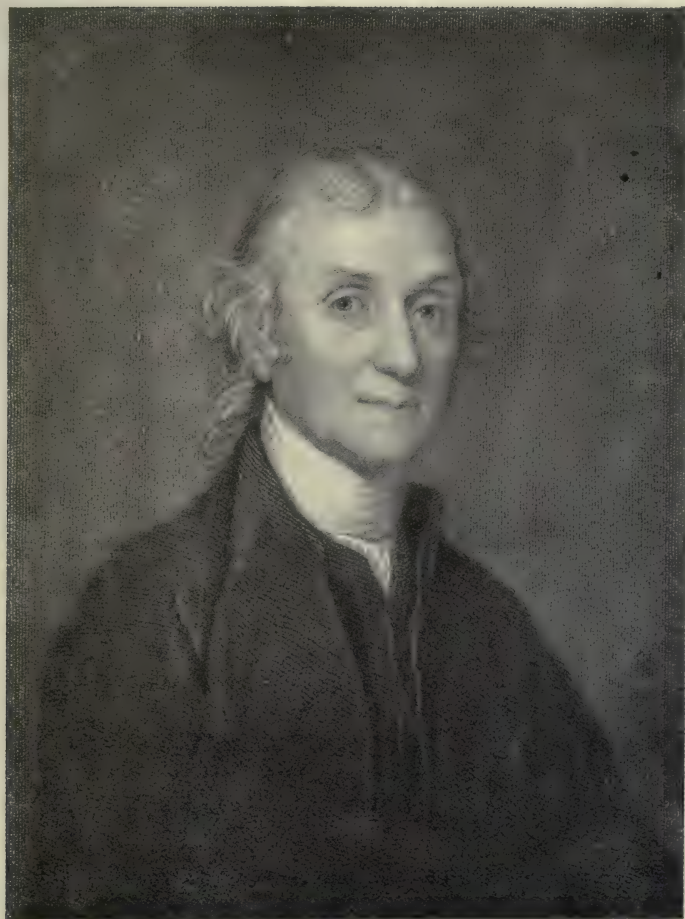
JOSEPH PRIESTLEY
B. England, 1733.   D. Pennsylvania, 1804.

CHAPTER IV

MIXTURE—ELEMENT—COMPOUND

The Law of Definite Proportions

38. **Mixtures and compounds.**—We have some roll sulphur which has been finely powdered and some copper filings. A small quantity of the copper is mixed carefully with about half its weight of the sulphur, and the mass examined. It is easily seen to consist of copper and sulphur, lying side by side, and this would at once inform us that it is a mixture of two substances. Now suppose the particles of copper and sulphur to be so small that, to the eye, the powder appears uniform. In this case the application of the microscope would reveal the presence of both. But suppose the particles of both to be so small that no microscope makes them visible. What then? How can we be sure that we have here a mixture of two substances and not a compound, which, of course, is *one* substance? Here we are driven to use methods of separating the copper from the sulphur.

39. **Separation of mixtures.**—For instance, it is easy to obtain a liquid heavier than the sulphur but lighter than the copper. When the mixture is thrown into this the sulphur floats and the copper sinks. Or we can shake up the mixture with water. Both sink, but the sulphur, being much lighter, remains suspended longer, and by pouring off at the right time, and repeating the " elutriation," as it is called, the two may be separated. Or, finally, we can treat the mixture with a liquid which dissolves one constituent and

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not the other. Thus *carbon disulphide,* a colorless inflammable liquid, dissolves sulphur freely and copper not at all, and when the mixture is stirred with it the sulphur dissolves and can be recovered by pouring off the liquid from the copper and allowing it to evaporate.

Now let the mixture of copper and sulphur be placed in a test-tube, and strongly heated at one point. There is a considerable evolution of light and heat. When the tube cools we break it, and find a bluish-black, uniform substance called copper sulphide, in which no copper and no sulphur can be perceived in any way, and, applied to which, the methods of separation, which succeed with the mixture, fail. For instance, if we powder the copper sulphide and throw it into a liquid whose density lies between that of copper and sulphur, no separation results. Copper sulphide is one substance, having its own density, and what happens depends entirely on whether the copper sulphide is lighter or heavier than the liquid. If heavier it will all sink; if lighter it will all float. Nor will carbon disulphide dissolve any sulphur from copper sulphide.

It will be seen that the distinction between a mechanical mixture of two different powders and a chemical compound of the same two substances is an easy one to make. The methods of separation depend upon the fact that the mixture consists of two solids lying side by side, and that the two solids have different properties. The next question is whether there are any bodies regarded as mixtures, upon which all these methods of separation fail; in other words, are there mixtures which can not be thought of as consisting of two bodies very finely divided and mixed—mixtures which are not only uniform to the eye, but really so. The student will at once think of mixtures of gases like the air, and of the various cases of solutions in liquids and solids which have been discussed. These are mixtures which are perfectly uniform, and the separation of which, by

methods like those which succeed with copper and sulphur, is usually impossible. Why, then, are bodies like glass, air, and salt water regarded as mixtures at all? Why not regard each as one substance—as a compound? The answer to this is simple and of supreme importance.

40. **The law of definite proportions.**—*A pure substance, whether an element or a compound, has always the same composition.* It has been pointed out that not the slightest variation in the proportions of hydrogen and oxygen in water can be detected. This is true of all compounds without exception, and it is the great distinction between them and mixtures. The statement is commonly called the *law of definite proportions.* We may express it again in this way: "*The composition of a pure chemical compound is constant.*"

We can now state another difference between the mixture and the compound of copper and sulphur. The mixture we can make in any desired proportions of the two. But the compound which we have made will always contain 126 parts of copper and 32 of sulphur, and we are powerless to produce the slightest alteration in these proportions.[1]

To sum up. Experiment reveals this remarkable fact, that there are certain forms of matter whose composition is constant. Chemists agree to name these substances *chemical compounds.* When they discover that the composition of a substance varies, they class it with the mixtures.

41. **Elements.**—In the first chapter we separated water into hydrogen and oxygen by passing the electric current through it. Mercuric oxide also we have split up into oxygen and mercury by heat. By various methods all chemical compounds can be decomposed, some by the current like

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[1] There is another compound of these two elements which contains half as much copper to the same quantity of sulphur—that is, 63 parts copper and 32 sulphur; but this is a different substance and does not affect the argument.

water, very many, most, in fact, by intense heat, like mercuric oxide. As a result of this separating process we find that we have obtained substances which resist all attempts to decompose them further. Chemists have never succeeded in separating mercury or oxygen or hydrogen into simpler forms of matter. All of the very numerous compounds which have been found in the earth's crust have been treated in this way, and as a result there have been obtained about eighty substances which, at present, can not be further decomposed. These are called *elements*. It is impossible to state the number precisely, because, owing to the great rarity of some of them, and to the imperfections of our methods, there are always some whose elementary character is in doubt.

42. **Meaning of the term "element."**—It is important to understand clearly the way in which the idea of " element " is arrived at. An element is simply a substance which, at present, can not be further separated. As we progress we shall discover examples of bodies once thought elements which turned out to be compounds when improved methods of separation were applied to them. Thus we are never in a position to assert that any substance will always resist the efforts of chemists to decompose it. All we can say is that it has thus far resisted those efforts. But if the elements are really compounds of hitherto unknown substances, then these substances are knit together far more firmly than the constituents of any ordinary compound. This is shown not only by the fact that they resist all attempts to split them up in the laboratory, but also by the work of astronomers, who have detected many of them in the atmospheres of the sun and other stars, where they resist temperatures far higher than those we can produce artificially.[1]

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[1] Recent results make the temperature of the sun about 6,000° C. Many stars are far hotter than this. The highest temperature we can produce in the laboratory does not exceed 3,500° C.

CHAPTER V

HYDROGEN

43. **Occurrence.**—*Hydrogen* compounds exist in the bodies of all animals and plants, and many of them are found in the rocks as minerals.

The gas itself is rare in nature. It has been found enclosed in meteors and in masses of rock-salt, it is contained in the natural gas of Pennsylvania and in the intestinal gases of animals, and is a product of the complex chemical process which we call putrefaction or decay. Hydrogen is continually being thrown into the atmosphere by the gases from volcanoes, and just what becomes of this hydrogen is a matter of great interest. We should expect it to accumulate, but it does not, for although even the pure air over the ocean contains a little of the gas, the quantity is very small. Its extreme lightness makes it appear probable that it escapes continually from the upper regions of the air into space, and so its accumulation is prevented.[1]

·44. **Preparation from sodium and water.**—Two methods of obtaining hydrogen from water have already been mentioned, the passage of the electric current and the application of intense heat. *Sodium* is a soft, wax-like metal, which must be kept under naphtha, as it is rapidly acted upon by air. A cylinder is filled with water and inverted in a dish

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[1] Enormous quantities of free hydrogen are contained in the atmosphere of the sun and other stars. These stars are immensely larger than the earth, and gravitation is sufficiently intense to prevent the hydrogen from escaping.

of water, and a small piece of sodium, which must be perfectly clean, is wrapped tightly in wire gauze, and the gauze,
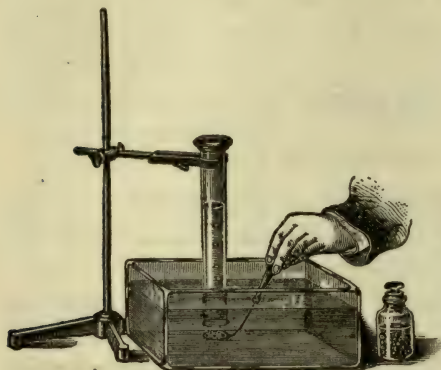

FIG. 8.—Hydrogen from water and sodium.

held in forceps, is introduced under the mouth of the tube (Fig. 8). Bubbles of a colorless gas rise into the tube. The sodium has disappeared and the water in the dish has acquired a soapy feel. This is due to the presence of sodium hydroxide, commonly called caustic soda, which is dissolved in the water, and which we could obtain as a white solid by evaporating the solution to dryness. Caustic soda is a compound of sodium, oxygen, and hydrogen. The sodium has combined with all of the oxygen and half of the hydrogen of the water, and the other half of the hydrogen has been liberated. Of course, only a small portion of the water has taken part in the change. The rest remains, and in it the sodium hydroxide is dissolved.

We can easily prove that the cylinder contains a combustible gas by taking it out of the water and bringing the open end near a burning match. A pale flame begins at the mouth of the cylinder and runs to the bottom. The hydrogen combines with oxygen from the air, and again exists as water.

FIG. 9.—Hydrogen from hydrochloric acid and zinc.

45. **From zinc and acids.**—Some zinc is placed in a beaker, and hydrochloric acid poured upon it. There is a violent

escape of gas, which, on being lighted, burns with a large pale flame (Fig. 9). The gas is hydrogen. Hydrochloric acid is a compound of hydrogen and chlorine and the zinc combines with the chlorine, producing zinc chloride, while the hydrogen escapes.

For preparing larger quantities of hydrogen, the apparatus shown in Fig. 10 is employed. It consists of a large bottle, closed by a doubly perforated rubber cork. Through one hole runs a tube which has a small funnel at the upper end. The lower end of this tube reaches nearly to the bottom of the bottle. The other hole carries a tube which
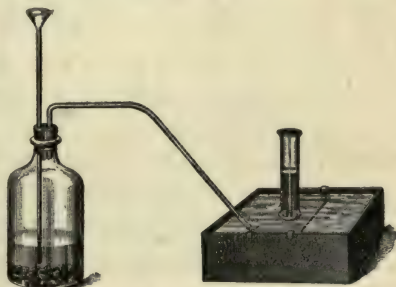

Fig. 10.—Preparation of hydrogen.

ends just inside the cork, and through it the gas is led away. In the bottle is placed some zinc covered with water, and sulphuric acid is poured through the funnel tube. At once evolution of hydrogen begins. This first quantity of gas mixes with the air in the bottle and produces an explosive mixture, so that it is necessary to wait until all the air is expelled from the apparatus before collecting or lighting the gas. The gas may be collected over water, as shown in the drawing.

46. **Physical properties.**—Hydrogen is a colorless, odorless gas. By cooling the strongly compressed gas to an extremely low temperature, and then permitting it to escape through a small orifice into an intensely cold vessel, it has been converted into a colorless liquid. When still more intensely cooled, it solidifies to an ice-like solid. The evaporation of liquid hydrogen produces the lowest temperature known to science, a temperature only about 13° above

the absolute zero of physics. When an empty test-tube is dipped into it, solid air at once collects in the tube. Liquid hydrogen is less than one-tenth as dense as water, and solid hydrogen appears to have about the same density as the liquid. The liquid is therefore by far the lightest of all liquids, and the solid of all solids. The gas is the lightest of gases, air being 14.39 times as heavy. It is very slightly soluble in water, 50 volumes of water dissolving 1 volume of the gas, at ordinary temperatures. It has been seen that hydrogen is extremely difficult to liquefy, and it is an interesting fact that this is the case with all gases whose solubility is very slight.

Hydrogen dissolves in various metals, in gold, silver, and platinum, for instance, and notably in palladium, a white metal somewhat similar to platinum. Palladium will dissolve about 1,000 times its volume of the gas. This power of hydrogen, of forming solid solutions with the metals, explains its ability to pass through thin plates of iron or platinum.

47. **Chemical properties.**—When a current of hydrogen is ignited where it escapes into the air it burns with a pale

Fig. 11.—Oxyhydrogen blowpipe.

blue flame, combining with the oxygen of the air to produce water.[1] It has been shown that some little hydrogen escapes from the flame into the air without being burned. When hydrogen burns in oxygen it produces the hottest flame which has been obtained, the oxyhydrogen flame. This melts platinum easily, and is used in working the metal into crucibles and dishes for
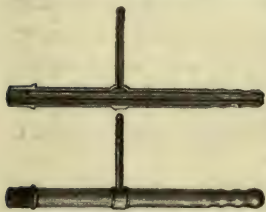
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[1] It is best to insert a short tube made of platinum foil into the glass tube, otherwise the flame is colored yellow by sodium from the glass.

chemical purposes. Solids—lime, for instance—which do not melt when placed in the flame, glow with a bright
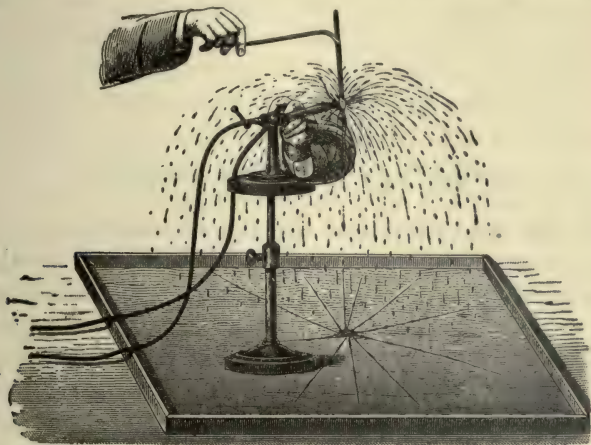

Fig. 12.—Burning of iron in the flame of the oxyhydrogen blowpipe.

light, the so-called lime-light or Drummond light. The apparatus usually employed for producing the oxyhydrogen flame on the lecture-table is represented in Figs. 11 and 12.

A cylinder, filled with hydrogen, is held open end down, and a lighted candle stuck on a stiff wire is pushed up into it (Fig. 13). The hydrogen is inflamed at the mouth of the cylinder, but the candle goes out in the gas. The burning of the candle is the combination of its constituents with the oxygen of the air, and, of course, this can not continue when the candle is surrounded by hydrogen. Hydrogen

Fig. 13.—Behavior of a lighted candle in hydrogen.

is not poisonous, but small animals placed in it suffocate, owing to the lack of oxygen, without which no animal life can continue.

CHAPTER VI

OXYGEN AND HYDROGEN PEROXIDE

48. **The free oxygen of the air.**—We may now study the other constituent of water. We have already obtained oxygen by the decomposition of water, and by heating mercuric oxide, as a colorless gas which causes a spark to burst into flame, and it has been pointed out that this is due to the fact that the air contains only about 21 per cent by volume of oxygen, and that the other constituents interfere with combustion. This free oxygen of the air is essential to all combustion processes, and to the life of all animals and most plants. Under the influence of sunlight the carbon dioxide of the air is decomposed in the green parts of plants, the carbon built up into the structure of the plant, and the oxygen returned to the air. If some sprigs of mint are placed in a flask which is filled with water containing carbon dioxide, then inverted and placed in sunlight, bubbles of oxygen collect in the upper part of the flask. But the roots and, in general, the portions of plants which are not green absorb oxygen from the air, and give off carbon dioxide. Thus, in a plant, two opposite processes occur together, one of which puts oxygen into the air and the other takes it out; but the first takes place on a far larger scale, and a plant, on the whole, absorbs carbon dioxide from the air and gives off oxygen. On the other hand, combustion processes and the life of animals make continual drafts upon the oxygen of the air, and discharge carbon dioxide into it.

If these two opposed influences were perfectly balanced, the percentages of oxygen and of carbon dioxide in the air would remain the same. Only slight variations with the seasons have been detected. Air in a vase discovered in the ruins of Pompeii, which had been sealed up for nearly two thousand years, was analyzed by Liebig, and was found to possess the same composition as the air which bathes the surface of the planet at present. But it would take a long time to produce a variation which could be detected, and we are by no means justified in assuming that the two processes in question exactly compensate each other, more especially as we know from geological facts that there was a period in the history of the earth when the plants obtained the upper hand, and produced an enormous decrease in the carbon dioxide and increase in the oxygen of the air. At present it is very probable that the pendulum has swung in the other direction, and that the immense combustion processes carried out by man are gradually increasing the carbon dioxide and decreasing the oxygen.

In spite of its importance, the quantity of oxygen in the air, about 21 per cent by volume and 23 per cent by weight, is small compared with that which exists in oxygen compounds. Water contains eight-ninths of its weight of oxygen, and a layer of water 264 centimeters ($8\frac{2}{3}$ feet) in thickness over the earth would contain as much oxygen as the atmosphere.

49. **Preparation.**—*Potassium chlorate* is a white crystalline compound of potassium, chlorine, and oxygen. When it is heated it first melts, and then gives off its oxygen, leaving *potassium chloride,* a compound of potassium and chlorine, behind. Since the potassium chlorate may explode when heated alone, it is usual to mix with it some substance which causes the oxygen to be given off more regularly, and at a lower temperature. Various substances possess this power. Finely divided platinum is one, but the material

commonly employed is manganese dioxide. The manganese dioxide is found unaltered after the experiment, mixed with the potassium chloride. It promotes the decomposition of the potassium chlorate, but remains unaffected itself. This is called a case of *catalytic action,* and this term is applied to all cases in which substances influence chemical changes into which they do not enter.

50. **Physical properties.**—The oxygen can be collected over water in which it is only slightly soluble. The apparatus is the same as that shown in Fig. 28.

Oxygen is a colorless, odorless gas. By great cold and pressure it is converted into a light blue liquid, which is somewhat denser than water, and is strongly attracted by the magnet. One hundred volumes of water at 0° and under one atmosphere pressure dissolve less than 5 volumes of the gas, so that the solubility is slight. All natural surface waters contain dissolved oxygen, and while the quantity is small it is important, for without it fish-life would be impossible. The dissolved oxygen can be extracted from water by boiling and cooling in the absence of air, or by means of the air-pump. In such water fish suffocate.

51. **Chemical properties.**—The combustions which occur in the air consist in the combination of carbon and hydrogen with the oxygen of the atmosphere. These phenomena occur far more energetically in pure oxygen than in air. At present oxygen is no longer made in large quantities on the chemical lecture-table, because the steel cylinders, full of the compressed gas, which are sold furnish a far more convenient source. From one of these we collect over water a number of jars full of oxygen. A little sulphur is placed in an iron spoon and heated in the air until it begins to burn feebly. When plunged into oxygen there is a great increase in the vigor of the combustion (Fig. 14). Charcoal, especially that made from bark, burns in it, throwing off showers of sparks. A steel watch-spring—steel we can consider

as a variety of iron—whose combustion has been started by a piece of wood split and slipped over the end, is converted into iron oxide, with brilliant scintillations (Fig. 15). Phosphorus and magnesium burn with blinding splendor, and with such intense evolution of heat that the jar is often fractured. In all these cases the products are the oxides of the elements employed, those of carbon and sulphur being colorless gases and those of phosphorus and magnesium white solids. In *absolutely dry* oxygen, charcoal and phosphorus can scarcely be induced to burn at all, and there are many other combustions which only take place in the presence of traces of water-vapor. We can now classify this action of water with the action of manganese dioxide on potassium chlorate as a case of *catalytic* action.

FIG. 14.—Combustion of sulphur in oxygen.

52. **Relation of oxygen to life.**—Free oxygen is essential to the life of animals. In its absence suffocation results.

FIG. 15.—Combustion of iron in oxygen.

Thus, when a small animal, like a mouse, is plunged into a jar of nitrogen, it dies at once; though the nitrogen is not at all poisonous, it kills by excluding the oxygen, without which life can not continue. The energy—heat and motion—which continually appears in the animal body during life has its source in the combination of the carbon and hydrogen of the tissues with the oxygen of the air. The products of this change are carbon dioxide and water, just as in combustions which take place outside the body. For this reason the air which

leaves the lungs has a very different composition from that which enters them. It contains more than 4 per cent by volume of carbon dioxide—about one hundred times as much as the inspired air—and has lost about 5 per cent of the oxygen.

	Oxygen.	Nitrogen and argon.	Carbon dioxide.	
Pure air.......	20.96	79.01	0.03	} Per cent by
Expired air....	16.03	79.59	4.38	} volume.

Carbon dioxide is eliminated and oxygen absorbed through the skin also, but the quantities are trifling.

Oxygen is essential to the higher plants, though death, when it is withdrawn, is far less rapid than with animals. It is an interesting fact that although oxygen is the constituent of the air which is most directly concerned with the life process, it is not able to support life alone. An animal supplied with the pure gas constantly renewed will die at length, though life continues for a long time.

Ozone

53. In the experiment with mercuric iodide we have met with a substance which can exist in two very different modifications. It will not surprise us, therefore, to learn that many of the elements possess the same power. Oxygen furnishes an interesting example of this.

54. **Preparation.**—For more than a century it has been known that the air near an electrical machine in operation acquires a peculiar odor. This is due to the fact that the oxygen of the air is transformed by electric discharges into another modification, ozone, which has a powerful smell. In order to prove this, it is best to employ pure oxygen, since otherwise it might reasonably be thought that the nitrogen, or some of the other constituents of the air, takes some part in the change.

Some starch paste is prepared by boiling a little starch with water in a dish. Into a small portion of this in a

test-tube throw a little powdered iodine. An intense blue color is produced, and this color always results when free iodine and starch paste come into contact. To the rest of the liquid a crystal of potassium iodide is added, and it remains colorless. Notice that iodine in the form of an iodide produces no color with starch paste, but, of course, anything which sets free the iodine will immediately produce the blue tint in the mixture. A long glass tube, *a,* sealed at one end, is filled with this liquid and inverted in more of it in a beaker, *b,* and some oxygen is passed up into the tube. There is no coloration, oxygen not having any action on potassium
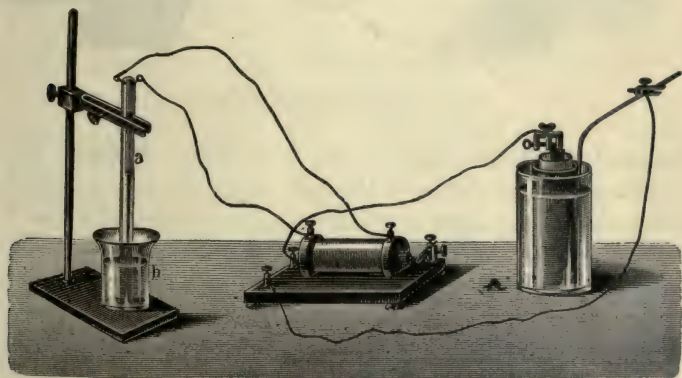
FIG. 16.—Transformation of oxygen into ozone by electric sparks.

iodide. This, of course, we might have predicted from the fact that the liquid remained colorless in the air.

Through the walls of the tube near the top there pass two platinum wires which enter opposite each other and do not quite meet in the center. These wires are now connected with an induction coil and a stream of sparks passed through the oxygen (Fig. 16). Gradually the blue color makes its appearance at the top of the liquid and spreads slowly downward. The sparks have transformed a portion of the oxygen into ozone, which attacks the potassium iodide and

liberates the iodine. The latter then produces the blue color with the starch. Far better than sparks for the production of ozone is the silent electric discharge. A wide tube is coated outside with tin-foil, and a narrow tube, which
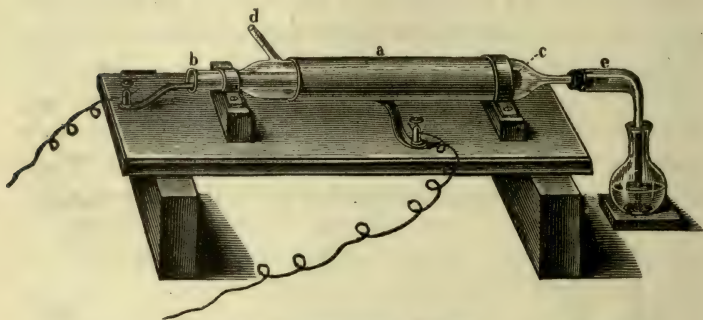

Fig. 17.—Preparation of ozone.

fits in it, is coated inside in the same way. Through the ring-shaped space between the two tubes oxygen is passed slowly from d to c, the coatings being connected at a and b with the induction coil (Fig. 17). The issuing gas contains large quantities of ozone, as well as much unchanged oxygen, from which it is best separated by intense cooling, when ozone containing only a little oxygen condenses. If the liquid is then allowed to warm a little, the oxygen vaporizes first and nearly pure ozone is obtained.

This method of preparing ozone is very important, because we have made it from oxygen without adding or subtracting anything except energy, and there is no escape from the conclusion that it is a variety of oxygen. There are many other methods of making it, but in all it is obtained mixed with large quantities of ordinary oxygen. Thus, when a stick of phosphorus is placed in a jar and partly covered with water, the air in the jar acquires the odor of ozone and will turn blue a paper which has been dipped in the solution of potassium iodide and starch (Fig.

18). When barium peroxide is acted upon by strong sulphuric acid, oxygen quite rich in ozone is given off, and can be identified by the odor, by the starch and potassium-iodide test and by its action on silver. It is sufficient to cover the test-tube with a clean silver coin when a dark stain of silver peroxide is produced upon it.

Fig. 18.—Ozone from phosphorus.

55. **Properties.**—Ozone is a colorless gas with a peculiar penetrating odor—the odor of phosphorus is due to it.[1] It is just $1\frac{1}{2}$ times as dense as oxygen. The density of oxygen referred to hydrogen is nearly 16; that of ozone nearly 24. Thus, when oxygen is converted into ozone, $1\frac{1}{2}$ liters is crowded into the space of one liter, or three liters of oxygen yield two of ozone. It is liquefied by cold and pressure more easily than oxygen, and the liquid is blue-black, magnetic, and extremely explosive. The explosion is the sudden conversion of the ozone into ordinary oxygen, a process in which energy is set free and increase of volume occurs.

56. **Change of ozone to ordinary oxygen.**—This change of ozone to oxygen occurs slowly at ordinary temperatures. If some ozone is sealed up in a glass bulb it is found, after a time, that the bulb contains ordinary oxygen. Heat greatly quickens the change. If a stream of oxygen containing ozone is passed through a glass tube gently heated by brushing it with a flame, the gas which issues will be ordinary oxygen and will produce no color upon the potassium-iodide starch-paper. On the other hand, at *extremely* high temperatures, oxygen changes to ozone. A large flask is filled with oxygen over water and a flame of hydrogen, led from a generator and burning at a platinum tip,

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[1] In thick layers ozone is blue.

is introduced. After a moment the flame is withdrawn, some of the solution of potassium iodide containing starch introduced, the flask closed and vigorously shaken. The blue color appears at once. The high temperature of the hydrogen flame has converted some of the oxygen into ozone.

57. Chemical properties.—Chemically, ozone has all the properties of oxygen. The combustions of charcoal, sulphur, phosphorus, and so on, which we have carried out in oxygen, will occur in ozone even more energetically, because the amount of heat evolved is greater. But ozone is far more active chemically than ordinary oxygen. It attacks and destroys organic matter like paper and rubber; blood becomes colorless in contact with it. Silver, which is not acted upon by ordinary oxygen at any temperature, is converted into black silver peroxide, and the production of this black stain on a polished silver surface is the most certain evidence of the presence of ozone we possess.[1] The reputation which ozone has obtained for health-giving qualities is entirely undeserved. In any considerable quantity the gas is violently poisonous, and even when very much diluted with air it is irritating and dangerous.

HYDROGEN PEROXIDE

58. Preparation.—*Barium peroxide* is a white compound of barium and oxygen. It has been remarked that when strong sulphuric acid acts upon it, oxygen containing ozone escapes. We have noted that sulphuric acid is a compound of hydrogen, sulphur, and oxygen. When it comes into contact with barium peroxide, the sulphur and the oxygen of the acid combine with the barium, producing a white solid called barium sulphate, which remains in the tube, the hydrogen of the acid unites with half of the oxygen of the peroxide, producing water, while the other half of the

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[1] Unfortunately this test is far from delicate.

oxygen escapes, partly as ozone. Now, when barium per-
oxide is slowly added to cold dilute sulphuric acid, barium
sulphate is produced in the same way, but no gas escapes.
In this case the hydrogen of the acid unites with *all* of the
oxygen of the barium peroxide, producing a compound which
must contain twice as much oxygen for a given weight of
hydrogen as water, and which is called *hydrogen peroxide*.
The barium sulphate, being insoluble in water, can be easily
got rid of by filtering the liquid, and the clear liquid which
passes through is a solution of hydrogen peroxide in water.

59. **Properties.**—Some of this liquid is allowed to fall
on a little manganese dioxide in a test-tube. There is a brisk
evolution of gas, which is found on trial to respond to the
spark test. Even when alone, hydrogen peroxide gives up
half its oxygen passing into water. This decomposition into
oxygen and water is very slow when it is preserved in the
dark and somewhat more rapid in the light. It becomes very
rapid when the hydrogen peroxide is heated or brought into
contact with manganese dioxide. Finely divided platinum,
gold, silver, or mercury produce the same effect. These are
further cases of what we have called " catalytic action,"
and it is interesting to notice that, in this case, *the effect
of the active substance is to increase very much the speed
of a chemical change which would nevertheless occur alone
if time enough were given. There is excellent reason to
believe that this is always the case, and that no substance
acting in this way can alter the final state of things, but
only the speed with which that final state is reached.*

We now pour some of our hydrogen peroxide on a little
lead sulphide, a black compound of lead and sulphur. Lead
sulphate, a white compound of lead, sulphur, and oxygen, is
produced. Most paints contain lead compounds, and the
blackening of oil-paintings with age is due to the forma-
tion of lead sulphide by the action of sulphur gases in the
atmosphere. Careful treatment with hydrogen peroxide

converts the dark lead sulphide into white lead sulphate and restores, in a measure, the original tints.

From all this it is clear that the additional quantity of oxygen in hydrogen peroxide is only loosely held; it easily yields it up to any oxidizable substance, passing into water at the same time, and thus it communicates oxygen to other substances, or acts as an *oxidizing agent*. Nevertheless, under some circumstances, it may remove oxygen, or produce *reduction*. Some silver oxide is placed in a beaker and hydrogen peroxide poured over it. There is a brisk evolution of oxygen, and metallic silver and water remain. In this case the loosely held oxygen of the silver oxide and of the hydrogen peroxide escape together. Hydrogen peroxide acts in a similar way with the oxides of gold and mercury.

The purest hydrogen peroxide is a thick colorless liquid, perfectly soluble in water, alcohol, and ether. Even in the cold, and rapidly when heated, it decomposes into water and oxygen, and, under the influence of heat, the decomposition frequently occurs with violent explosion. When water evaporates in the air a small quantity of it combines with the oxygen of the atmosphere, producing hydrogen peroxide. For this reason, traces of hydrogen peroxide are always contained in the atmosphere, and in rain-water and snow.

The water solution of hydrogen peroxide is a colorless transparent liquid. It is largely used for bleaching, and in surgery for washing wounds.

CHAPTER VII

COMBUSTION

60. SULPHUR, and especially phosphorus, combine slowly with oxygen at ordinary temperatures. In the case of sulphur no evolution of light or heat can be detected. Phosphorus is luminous in the dark owing to this gradual oxidation. When either substance is heated, the combination becomes more and more rapid. *This is usually the effect of raising the temperature; to increase enormously the speed with which a chemical change takes place.* Finally, if the burning substance is plunged into oxygen, there is a still further increase in the rapidity of the process. Now in all these cases the total amount of heat produced by the combination of a given weight with oxygen is exactly the same. In the same way, when a metal rusts, slowly forming its oxide in a process requiring years, the same amount of heat is produced as though it burned in oxygen in a few seconds, provided only that the product is the same in both cases. The only difference is that, in the first case, the evolution of heat is very slow, it is dissipated as fast as produced, and there is no perceptible elevation of temperature. But, in the second case, the energy is evolved in a few seconds, the substances are intensely heated, and the striking phenomena of combustion appear. The key to all this is the increase in the speed of the change with rising temperature. For, as soon as the change produces heat too rapidly for it to be dissipated, this heat will accumulate and raise the temperature of the substances.

This will produce an increase in the speed of the change, which will in turn produce more heat and a higher temperature, and so on.

61. Ordinary combustion consists in the rapid combination of various substances with the oxygen of the air. Such substances are called combustible. A gas, like oxygen, which permits them to burn, is said to support combustion; and this language is applied to any gas which permits the same substances to burn in it. Chlorine gas—one of the constituents of common salt—combines with phosphorus and other substances, producing light and heat, and is usually called a supporter of combustion. It is very desirable to perceive that whether a substance will burn or not depends entirely on what particular gas surrounds the substance at the time the experiment is made; and that

Fig. 19.—Apparatus for combustion in hydrogen.

whether a gas "supports combustion" or not depends upon the substance we try to burn in it. We have seen that a candle becomes incombustible in an atmosphere of hydrogen (p. 39).

A convenient apparatus for experiments on this subject consists of an ordinary lamp-chimney closed below by a rubber cork. Through the cork passes a glass tube, by means of which a current of hydrogen [1] is introduced from a generator or from a cylinder of the compressed gas (Fig. 19). The open top of the chimney is covered with a piece

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[1] The use of a hydrogen generator can be avoided by using common illuminating gas directly from the mains. This serves the same purpose as hydrogen in these experiments.

of asbestos cardboard, *a*, having a hole in the center through which the gas issues, and where it can be lighted to avoid its escape into the air. We have, then, in the chimney an atmosphere of hydrogen, and we can conveniently investigate the behavior of various substances by heating them in iron deflagrating spoons and introducing them into the hydrogen through the hole in the asbestos plate.

62. **Combustions in hydrogen.**—First, let some *turpentine* be started burning in the air and then plunged into the hydrogen. The flame is extinguished. Like the candle, turpentine is composed of carbon and hydrogen and can not continue burning in a gas which does not supply the necessary oxygen. On the other hand, some *nitric acid,* placed in a spoon and heated, simply boils in the air, but placed in the hydrogen, catches fire and burns with a pale yellow flame. The nitric acid is rich in oxygen, and the burning is the combination of this with the hydrogen to form water. But the most striking results are obtained with the metallic *chlorates.* Potassium chlorate has already been referred to as a compound of potassium, chlorine, and oxygen. The other chlorates are similarly constituted. They all contain a metal, chlorine, and much oxygen, and the oxygen is only loosely held. They may be placed in the spoon, heated in the air, and plunged into the hydrogen, where they burn with intense light-display, the flame having a color which depends on the particular chlorate employed. With potassium chlorate it is violet, barium chlorate a brilliant green, while sodium chlorate gives a yellow, and strontium chlorate a red flame of blinding brightness. These are the flame colors of these metals— that is, any volatile compound of the metal, introduced into the Bunsen flame, will produce the corresponding color, violet for potassium, yellow for sodium, and so on.

63. **The nature of flame.**—From these experiments we perceive that in an atmosphere of hydrogen the ordinary

phenomena of combustion are reversed: substances rich in carbon and hydrogen become incombustible, and substances rich in loosely held oxygen burn brilliantly. The next step is to inquire into the nature of flame. What is a flame and under what conditions will a substance burn with flame? We have already met with cases of both kinds of combustion. Thus, sulphur, phosphorus, and magnesium burn in oxygen with flame, while iron and charcoal burn brilliantly, but without flame. A flame is a mass of highly heated gas or vapor; it is the portion of space in which a chemical combination is occurring with great evolution of heat, both parties to the combination being gases or vapors at the temperature of the experiment.

Iron and charcoal burn without flame because they are not vaporized, and the process can only occur at the surface of the iron or the charcoal. Magnesium burns with flame, because at the high temperature it is vaporized and the vapor passes into the space immediately surrounding the burning wire. Thus, the combination does not take place at the surface of the wire, but in the adjacent space, and there is produced an intensely heated mass of magnesium vapor, oxygen, and magnesium oxide, which make up the flame.

Sulphur and phosphorus behave like magnesium. So with a candle, the wax is melted and drawn up by the wick. Approaching near the heat, it is converted into a mixture of combustible gases and vapors; and these burn with a flame. It will be clear from all this that *any gas or vapor which burns at all will burn with a flame, while a solid will burn with flame only when it is volatilized at the temperature of the experiment.*

We may now use the lamp-chimney to exemplify another interesting fact. If any gas A will burn in a gas B, then B will also burn in A under the proper conditions. A tube ending in a fine jet—the ordinary mouth blow-pipe

is convenient—is connected with a cylinder of compressed oxygen, and a very gentle stream of oxygen allowed to escape. The tube is now intro- duced through the flame of burning hydrogen into the chimney. The oxygen catches fire from the hydrogen flame and goes on burning in the chimney with a pale blue flame exactly like that of hydrogen burning in oxygen (Fig. 20). It is easy also to produce a flame of air burning in hydro- gen. In order to do this, place in the bottom of the chimney a rubber cork having *two* holes,

Fig. 20.—Combustion of oxygen in hydrogen.

one of which carries the hydrogen tube, *a,* and the other a short rather wide glass tube, *b,* open at both ends. With-

Fig. 21.—Combustion of air in hydrogen.

draw the cork a moment, light the hydrogen at its tube, and insert the cork in its place. The hydrogen flame soon exhausts the supply of oxygen in the vessel, a pale blue flame floats about the chimney for an in- stant, then settles on the open tube, where it continues to burn. This is the air-flame (Fig. 21).

We may now light the hydro- gen above at the hole in the as- bestos plate, and we have above a flame of hydrogen burning in air, below a flame of air burn-

ing in hydrogen. The latter can be extinguished instantly by stopping the lower end of the air-tube with the finger.

64. **Structure of flame.**—Into the flame of a candle we introduce one end of a glass tube open at both ends. When
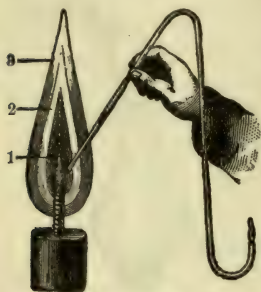
FIG. 22. — Structure of candle-flame. *1*, interior composed of unburned gases; *2*, luminous portion; *3*, outer mantle, when complete combustion takes place.

the tube is inclined upward, gases rise through it and may be lighted at the end, where they burn with a luminous flame (Fig. 22). This experiment—due to Faraday—shows that the candle flame is hollow. This is true of all flames. The hydrogen flame contains an inner dark cone, consisting of unburned gas, and an outer faintly luminous sheath which is the portion of space in which combustion is taking place. The question why the hydrogen flame is only faintly luminous, though very hot, while the candle or gas flame gives off a bright light, has been much discussed, but no final answer has

FIG. 23 A.—The Bunsen burner. *e e*, chimney; *d*, holes for admission of air.

been given. It is possible that the combustible gases in the latter case are decomposed by the heat

FIG. 23 B.—Burner with chimney removed. *a b*, base; *d*, gas-supply; *c*, aperture for admission of air.

with separation of solid carbon and then these fine solid particles, being intensely heated, glow brightly.

65. **The Bunsen burner.**—The coal-gas flame can be made non-luminous by depressing a flat-iron or other cold metallic object upon it. In the same way, when much nitrogen is mixed with the gas before it is burnt, the flame becomes blue by simple cooling. When oxygen is mixed with the gas, the disappearance of the light is due to a different cause. The flame becomes much hotter, but combustion is so perfect that no carbon separates and no glowing can occur. In the Bunsen burner, air is drawn in through the holes around the base, a mixture of gas and air ascends the tube and burns at the top, and the lack of luminosity is probably due to both causes acting together: to the dilution of the flame by the nitrogen and the greater perfection of combustion brought about by the added oxygen. The student will best understand the action of the burner by taking it apart and examining it with some care (Fig. 23).

CHAPTER VIII

NAMING CHEMICAL COMPOUNDS—CHEMICAL SYMBOLS AND EQUATIONS—DIFFERENT KINDS OF CHEMICAL CHANGE

66. The names of chemical compounds.—Returning now to the combustions in oxygen carried out in the sixth chapter, we have seen that the process consists in the rapid production of the oxide of the element employed. The termination " ide " generally indicates a compound of two elements. Thus, an oxide consists of oxygen in combination with some other element; mercuric oxide consists of mercury and oxygen. In the same way a sulphide contains sulphur combined with something else; lead sulphide is a compound of lead and sulphur. The same nomenclature is applied to other elements. Sodium chloride, common salt, is a compound of sodium and chlorine; calcium carbide, used in certain bicycle lanterns, a compound of calcium and carbon, and so on.

If an element forms more than one oxide, it is necessary to distinguish them in some way by name. Thus, there are two compounds of mercury with oxygen. One, mercuric oxide, contains 200 parts of mercury and 16 of oxygen, the other 400 parts of mercury and 16 of oxygen. The first we have already learned to call *mercuric* oxide, the second is black and is called *mercurous* oxide. There are two compounds also of mercury and chlorine. One, the well-known medicine *calomel*, contains 200 parts of mercury and 35.5 parts of chlorine. This is *mercurous* chloride. The other —*corrosive sublimate*—contains 200 parts of mercury and

twice 35.5, or 71 parts, of chlorine. It is called *mercuric* chloride.

It will be seen from this that the ending " ous " is applied to that compound which contains less of the element coming last in the name of the compound. Mercurous bromide contains less bromine than mercuric bromide, cuprous sulphide less sulphur than cupric sulphide.

67. **Description of the composition of compounds by formulas.**—Water contains 2 parts of hydrogen and 16 of oxygen by weight. Let us agree to represent 1 part of hydrogen by the symbol H. Then 2 parts can be represented by the expression H_2. Similarly, 16 parts of oxygen by weight can be represented by the symbol O. Then the composition of water can be briefly described by the *formula* H_2O, which means 18 parts of water, containing 16 of oxygen and 2 of hydrogen. It makes no difference what particular unit of weight we employ, for the proportions are relative only, but it will fix our ideas to think of some definite unit, and, since the gram is universally employed in science, we shall use that.

There are 453.6 grams in a pound, so that the gram is a little less than the $\frac{1}{28}$ of an ounce. The formula H_2O, then, means 18 grams of water, of which 2 grams are hydrogen and 16 grams oxygen. Mercuric oxide we have seen to contain 200 parts of mercury and 16 of oxygen. Let us represent 200 parts of mercury by the symbol Hg. Then the formula HgO is a concise description of the composition of the substance. It signifies 216 grams of mercuric oxide, of which 200 grams are mercury and 16 oxygen. Mercurous oxide contains 200x2, or 400 grams of mercury and 16 of oxygen in 416 grams. The formula becomes Hg_2O. So the symbol Cl is employed to signify 35.5 parts by weight—grams, for example—of chlorine. It has just been mentioned that calomel, mercurous chloride, contains 200 parts of mercury and 35.5 of chlorine. Clearly

the formula is HgCl. Mercuric chloride—corrosive sub-limate—which contains 35.5x2, or 71 parts of chlorine to 200 of mercury, must be described by the formula $HgCl_2$. Similarly, the symbol of sodium is Na, and the weight which experience has shown to be most suitable for de-scribing the composition of sodium compounds is 23. NaCl is the formula of table salt, and this means that in 58.5 grams of it there are 23 grams of sodium and 35.5 of chlorine.

68. **Symbols and their meaning.**—Now it is found that by means of the symbol H, meaning 1 part of hydrogen by weight, the composition of all hydrogen compounds can be briefly described in formulas. So the symbol O, meaning 16 parts of oxygen, enables us to write simple formulas like H_2O for water, HgO for mercuric oxide, Hg_2O for mer-curous oxide. We shall find as we progress that by means of this symbol the composition of all compounds containing oxygen can be described. It is, we may say, a natural chem-ical unit in which oxygen enters into its compounds, and while we often have to multiply it in order to express the composition of a compound, it is never necessary to divide it. In the same way, by means of the symbol Hg, mean-ing 200 parts of mercury, the composition of all mercury compounds without exception can be described. Similarly with Cl = 35.5 parts of chlorine, and Na = 23 parts of sodium. The composition of every known compound of these elements can be described by simple formulas based upon these quantities.

69. **The atomic weights.**—There is for every element a natural quantity in which it enters into its compounds, and by means of which concise descriptions of the composition of these compounds can be given. These numbers are given in the table in the appendix and are called the " atomic weights " of the elements. This term is derived from the hypothesis that material things are composed of small par-

ticles with vacant spaces between, a view which has been helpful, especially in dealing with the very numerous compounds which carbon forms with other elements. It will be discussed later. At present it is important for the student to perceive that everything which has been stated is pure fact, and is quite independent of any speculation of this kind.

70. **Chemical equations.**—We can now proceed to describe chemical changes in the same kind of language. When by heating mercuric oxide it separates into mercury and oxygen, we write: $HgO = Hg + O$, which means that 216 parts of mercuric oxide separate into 200 of mercury and 16 of oxygen. In the same way the decomposition of water by the current can be written: $H_2O = H_2 + O$, signifying that 18 grams of water produce 2 of hydrogen and 16 of oxygen. The decomposition of potassium chlorate by heat is somewhat more complex. Its formula is $KClO_3$, which, of course, means 39 parts of potassium, 35.5 of chlorine and 16x3, or 48 parts of oxygen, in combination. When it is heated the change is represented by the expression: $KClO_3 = KCl + 3O$, the 48 parts of oxygen escaping, while the potassium and chlorine remain together, as 74.5 parts of *potassium chloride*. An expression of this kind is called a *chemical equation*. It is simply a description of a chemical change, in a kind of language which, for clearness and brevity, has probably never been equaled. The sign of equality in the equation stands for the law of the indestructibility of matter. Since nothing is lost or gained, it stands for equality in weight.

The total weight of the substances entering into the change—those on the left-hand side—must be equal to the total weight of the products—those on the right-hand side of the sign of equality. Further, *no element has ever been transformed into any other element*. This great principle is the most important result of fifteen hundred years of un-

successful efforts by the alchemists to transform copper, mercury, lead, and other cheaper metals into gold and silver. Our chemical equations must conform to it. Since every symbol represents a fixed quantity of some element the number of symbols corresponding to each element must be the same on both sides. Thus, in the equation for the decomposition of potassium chlorate, we have on each side one K, one Cl, and three O. This equation satisfies our two laws therefore; the law of the indestructibility of matter and that which expresses the impossibility of mutual transformation of the elements, and any equation which violates either principle is absurd by inspection.

An equation must be a faithful description of a real process. It is easy to write equations which satisfy both the laws mentioned above and yet are false because the change which they describe does not really happen. The equation $KClO_3 = KClO + O_2$ is a case of this kind. So far as the number of symbols on each side is concerned, it is correct, for we have on each side one K, one Cl, and three O, but since the compound KClO is not, as a matter of fact, produced when potassium chlorate is heated, the equation is false. In the same way every correct chemical formula, like HgO, NaCl, and so on, represents the composition of a real chemical compound. Of course, the formula can not be written until the compound it describes has been prepared in the pure state and analyzed. It is, in fact, one way of writing the result of a chemical analysis of the compound.

71. **Different kinds of chemical change.**—When magnesium burns, two substances, magnesium and oxygen, disappear, and one substance, magnesium oxide, is produced. A chemical change of this sort is called a *combination*. Other examples of combination are the union of copper and sulphur to copper sulphide (p. 32) and of hydrogen and oxygen to form water (p. 7).

Combination is the union of two or more substances to produce one substance.

On the other hand, when the electric current is caused to pass through water, the water separates into hydrogen and oxygen. This is the reverse of combination and a change of this kind is called a *decomposition.* The splitting up of mercuric oxide into mercury and oxygen (p. 26) and of potassium chlorate into potassium chloride and oxygen (p. 41) are examples.

Decomposition is the separation of one substance into two or more.

" If the elements should cease to form compounds with each other, what would be the result. All chemical compounds would be decomposed, and there would only be about eighty different kinds of substances. All living things would cease to exist, and in their place we should have three invisible gases and something very like charcoal. Mountains would crumble to pieces, and all water would disappear, giving two invisible gases. The process of life in its many forms would be impossible." (Remsen.)

There are other important kinds of chemical change which we shall become familiar with as we meet examples of them farther on in our work.

CHAPTER IX

SALT AND SODIUM

72. Synthesis of salt.—A fragment of sodium is placed in a bulb blown on a piece of hard glass tubing, and chlorine gas is passed through the bulb. On being gently heated, the sodium catches fire in the chlorine and burns with a dazzling yellow flame. When the bulb has cooled, we open it and find a white powder which the taste shows to be common salt (Fig. 24). Thus we have shown, by synthesis, that salt is a compound of sodium and chlorine.[1] Its formula is NaCl.
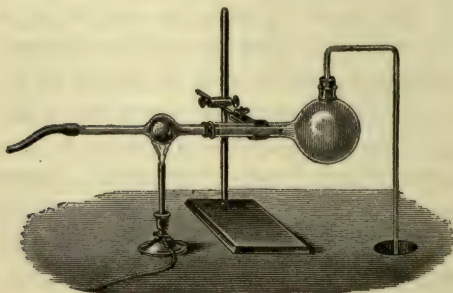
Fig. 24.—Synthesis of salt.

73. Occurrence of salt. — Seawater.—Salt is the most abundant compound of sodium as well as the most abundant compound of chlorine, and it is important because it is the raw material of two great groups of chemical industries, those of sodium and its compounds, and those of the compounds of chlorine. When 100 grams of the water of the open sea are evaporated to dryness, 3.5 grams of solid matter are left, of which more than 2.5 grams are

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[1] This is another interesting case of the catalytic action of water. Perfectly dry chlorine does not act visibly upon sodium.

sodium chloride. The rest consists of a great variety of substances.

Since the ocean receives the washings of the entire crust of the earth, and since everything is soluble in water to a greater or less extent, it is probable that sea-water contains all the elements. Nearly half of them have already been detected in it, mostly in very small quantities. The calcium of ocean-water must be mentioned, on account of its importance to the life of shell-fish; magnesium is present in considerable quantity, bromine in small proportion, but enough to make its extraction profitable under certain conditions.

Sea-water does not appear to contain any dissolved iodine compounds. The iodine, which it always contains, is present in suspended seaweed spores and is removed by filtering. The larger seaweeds also contain iodine.

Of course, sea-water dissolves gases from the air, oxygen, nitrogen, and carbon dioxide, and these are important to the life of fishes and marine plants. Many of the other elements are present in traces which require the most refined methods of chemical analysis to detect them. Among these we may mention iron, silver, and gold.

74. **Water of inland seas.**—In an inland sea supplied by streams and only losing water by evaporation, the quantity of dissolved matter may become very great, for the water which enters contains dissolved solids, and that which leaves contains none. This is the state of the Great Salt Lake and the Dead Sea. One hundred parts of the water of the latter, when evaporated, leave nearly 23 parts of solid residue, consisting chiefly of the chlorides of magnesium, calcium, and sodium, and there are other lakes whose waters contain as much as 30 per cent of material in solution. In all water of this kind marine life is impossible.

75. **Commercial production of salt.**—In Siberia some salt is obtained from sea-water by freezing. The ice which sep-

arates is fresh. It is removed, and the freezing continued until the solution of salt becomes strong enough to boil down profitably. Salt is obtained in warm climates, especially on the shores of the Mediterranean, by natural evaporation. Sea-water is allowed to run into shallow basins in which it evaporates of itself until the salt crystallizes out. Rock-salt beds have probably been produced by the cutting off of arms of the sea from the main body, during the geological past. Evaporation would then occur, and the end result would be a bed of salt which might become covered with a water-tight layer of clay, and so be protected from the dissolving action of the rains.

England produces more salt from rock-salt beds than any other country, and there are deposits in Austria and Germany and in various parts of the United States, for instance in southwestern New York.

76. Salt springs.—In the same districts occur salt springs. The evaporation of such natural brine, or of artificial brine made by turning water into a boring in a salt bed, is the most important source of salt. The water must contain at least 16 per cent of salt in order to be evaporated profitably. It is boiled down in iron pans until the salt separates.

77. Properties of salt.—Rock salt is often colored blue or yellow, but pure sodium chloride is colorless. It crystallizes in cubes. It dissolves in about twice its weight of water, and the solubility increases only very slightly when the liquid is heated. It is almost insoluble in alcohol. At a red heat it melts and at a slightly higher temperature rapidly vaporizes. This can easily be seen by sprinkling some salt on a hot fire.

78. Function of salt in the diet.—Salt is always used by civilized man at the table, and there has been some question as to whether it is a mere flavoring material, like pepper, or is a necessary element in a healthful diet. The facts

seem to favor the latter statement. The gastric juice
always contains a little hydrochloric acid, HCl, and this
is formed from the salt of the food. Experiments on
dogs have shown that, when the body is deprived of salt
for a long time, this hydrochloric acid disappears and the
functions of the stomach are no longer rightly performed.
Other chlorides can serve the same purpose as sodium
chloride in the diet. There are African tribes which em-
ploy potassium chloride, KCl, in a similar way. Salt, in
enormous quantities, acts as an irritant poison. In one
case 250 grams (about one-half pound), taken at one time,
caused death.

79. If a dilute solution of sodium chloride is cooled in a freezing
mixture and stirred with a thermometer, it is found to begin to
freeze at a lower temperature than pure water, and the ice which
separates is fresh. Now let the cooling be continued. For a while
ice continues to separate. Finally, there comes a time when the
remaining liquid freezes as a whole, ice and salt separating together.
From the moment the first crystal of salt separates along with the
ice the temperature remains constant until the whole mass has be-
come solid.

Most solutions behave in this way. When they are cooled, pure
ice separates first, and the temperature falls until the separation of
solid dissolved substance begins. Then the temperature remains the
same until the solidification is complete. Solutions in liquids other
than water act similarly.

In the same way, if a salt solution is heated, it begins to boil at a
higher temperature than pure water. The vapor of water is given off
and this leaves behind it a stronger solution. Now, the stronger the
solution the higher the boiling point, so that the temperature rises.
Finally, the continued loss of steam leaves the solution saturated,
and solid salt separates. From this moment the temperature is
fixed until the solution has been evaporated to dryness. This leaves
solid salt, which, of course, can be heated to any desired degree.
This behavior also is common to most solutions.

Sodium

80. Historical.—In discussing hydrogen, it has been remarked that when sodium acts upon water it liberates half of the hydrogen and combines with the other half and with all the oxygen, forming a compound called sodium hydroxide. We can now describe this process in symbols.

$$Na + H_2O = NaOH + H.$$
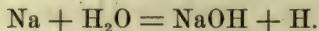
The substance which has the composition NaOH—sodium hydroxide—is familiarly called concentrated lye or caustic soda. It was for many years supposed to be an element, but in 1807 Sir Humphry Davy announced that when the electric current is caused to pass through a mass of moistened caustic soda, small globules of metal collect at the negative pole. From this he concluded that caustic soda was a compound containing a metal, and proposed for this metal the name *sodium*.

81. Preparation of sodium.—After trying many other methods, chemists have finally returned to a modification of Davy's process as the best for making sodium on a commercial scale. The current from a dynamo is passed through caustic soda, heated just to melting in an iron vessel. Oxygen is liberated at the positive pole and hydrogen and sodium together at the negative pole:

$$NaOH = Na + O + H.$$
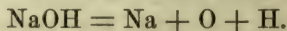
Many attempts have been made to prepare sodium by the action of the current upon salt, which is far cheaper than caustic soda. So far the methods have not succeeded in practice, but the efforts still continue and may at any time be successful.

82. Occurrence of sodium compounds.—Sodium chloride is the most common compound of the metal, but other sodium compounds are abundant in nature. Sodium nitrate,

SIR HUMPHRY DAVY
B. England, 1778.   D. 1829.

$NaNO_3$, occurs in great deposits on the western coast of South America. Most of the common rocks contain sodium compounds. It stands seventh among the elements in point of abundance, and recent calculations show that the accessible portion of the earth's crust contains about $2\frac{1}{3}$ per cent of it.

83. Properties.—Sodium is a metal with a brilliant, somewhat pink luster, which it instantly loses in the air. This is due to the fact that the water-vapor in the air acts upon it in just the same way that liquid water does, converting the surface into sodium hydroxide. Sealed up in a glass tube, from which the air has been removed by a current of dry hydrogen, the luster is permanent. It is soft like wax, can be cut readily with a knife, and is an excellent conductor of electricity and heat.

Heated in the absence of air, it melts to a mercury-like liquid, which, when further heated, passes into a purple vapor. Heated in air or oxygen, it burns with a yellow flame.

84. Oxides of sodium.—Two oxides can be produced according to the circumstances. If the temperature is high and the supply of oxygen small, the product is *sodium monoxide*, a gray substance, of the composition Na_2O. When this substance is sprinkled with water, it combines violently with it, producing sodium hydroxide:

$$Na_2O + H_2O = 2NaOH.$$
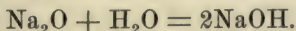
If, on the other hand, sodium is heated to a low temperature with abundant air supply, the product is yellow *sodium peroxide*, Na_2O_2. This is made on a large scale in this way, and is used for bleaching, because, when treated with a dilute acid, it yields a solution containing hydrogen peroxide. Hydrogen peroxide has the formula H_2O_2, and it differs from water, therefore, in containing 32 parts of oxygen instead of 16, in combination with 2 parts of hydrogen.

Its production from sodium peroxide and hydrochloric acid is represented thus:

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2.[1]$$
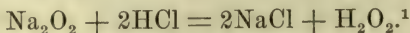
85. Sodium hydroxide, $NaOH$, can be obtained pure by treating sodium with water in a silver dish:

$$Na + H_2O = NaOH + H.$$
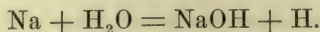
Since the action is violent, only a small fragment of the metal is brought into contact with the water at once. The liquid is finally evaporated to dryness and the residue melted. This method is employed in the laboratory, but it is far too expensive for the preparation of the vast quantities of sodium hydroxide which are made industrially. Practically, it is made from washing soda, sodium carbonate, Na_2CO_3. This is dissolved in water and the liquid boiled with slaked lime, calcium hydroxide $Ca(OH)_2$, in iron vessels. The reaction which takes place is expressed by the equation

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$
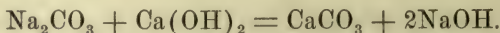
Calcium carbonate, $CaCO_3$, is the same thing, chemically, as marble or chalk. It is insoluble in water and settles to the bottom, so that the clear solution of sodium hydroxide can be poured off from it. This is then evaporated to dryness, melted, and cast into sticks. Chemists are actively at work on the problem of producing sodium hydroxide directly from salt by the electrical method, and it is probable that this method will be perfected and will displace the other in the near future.

86. Properties.—Sodium hydroxide is usually sold in the form of sticks. It is a tough, white, translucent mass,

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[1] Of course the formulæ HO for hydrogen peroxide and NaO for sodium peroxide would represent exactly the same composition by weight. The reasons for using doubled formulæ will be given later.

which can be melted and vaporized without decomposition. It is very soluble in water, and the solution has a slippery feel, because it acts chemically upon the oil of the skin, producing a soap.

87. **Deliquescence.**—When a stick of sodium hydroxide is allowed to remain exposed to the air, it becomes wet, because water-vapor is attracted from the air and the solution of sodium hydroxide is formed. Many other substances behave similarly, and this occurrence is called *deliquescence.* Whether a substance attracts water from the air and dissolves in this water depends entirely upon how much water the air contains at the time. Any soluble substance will deliquesce when the air is saturated with water-vapor. It is a familiar fact that table salt, which is not deliquescent ordinarily, becomes deliquescent at the seashore on account of the large quantity of moisture in the air.

88. **Uses of sodium hydroxide.**—Sodium hydroxide is a commercial product of great importance. It is used in enormous quantities for the production of soap, which is made by boiling caustic-soda solution with some oil or fat. In the case of castile soap, olive oil is used, palm oil for palm soap, and, for cheaper soaps, animal fats. Sodium hydroxide and its solution absorb carbon dioxide gas, CO_2, greedily from gaseous mixtures containing it, and are employed in the laboratory for this purpose. In this reaction the sodium hydroxide passes into sodium carbonate,

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$
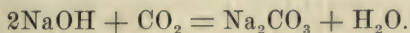
89. **Sodium carbonate,** Na_2CO_3, called soda or washing soda, is made from common salt by methods which can not be fully discussed here. One process consists in dissolving the sodium chloride in water and passing into the solution first ammonia gas, NH_3, and then carbon dioxide, CO_2. This is the equation,

$$NaCl + CO_2 + NH_3 + H_2O = NaHCO_3 + NH_4Cl.$$
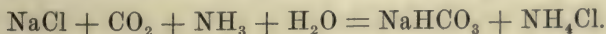
The substance $NaHCO_3$, called mono-sodium carbonate because it contains only one atomic weight of sodium, is ordinary *baking-soda*. Not being very soluble in water, it separates as a white powder, which can be converted into sodium carbonate, Na_2CO_3, by heat,

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$
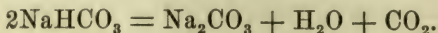
The carbon dioxide liberated in this change is used again in treating more sodium chloride. The substance having the composition NH_4Cl, which is the other product of the treatment of the sodium chloride, is called sal-ammoniac or ammonium chloride. We shall study it later, but it is necessary to remark now that the ammonia can be obtained from it again, and used over and over.

Sodium carbonate is a white powder, which melts at a red heat, and vaporizes undecomposed at a higher temperature. It has a bitter, nauseous taste, and is soluble in about five times its weight of water at ordinary temperatures. It is much more soluble in hot water, and when a hot, strong solution is cooled, there separates not the white powder which was originally dissolved, but colorless crystals, which can be obtained quite large by slow cooling. If one of the crystals is dried carefully with blotting-paper and heated in a dry test-tube, it will again be converted into the white powder, and much water will condense in the cold upper part of the tube. By making a similar experiment with a weighed quantity in a platinum dish, it can be shown that the quantity of sodium carbonate indicated by the formula Na_2CO_3 (106 parts) is in combination in the crystals with 180 parts of water, ten times the quantity represented by the formula H_2O. Hence we write the formula of crystallized sodium carbonate $Na_2CO_3 10H_2O$. This is the washing-soda of the household.

90. **Water of crystallization.**—Water in this condition, chemically combined with a salt, is called *water of crystal-*

lization. When it is driven out the crystal falls to pieces. The same salt may, and usually does, form several compounds with water in different proportions. Several are known in the case of sodium carbonate, of which one, $Na_2CO_3.H_2O$, is becoming an important technical product. Many other liquids play a similar *rôle.* Thus we have alcohol of crystallization, chloroform of crystallization, and so on. Some substances, salt and potassium chlorate, for instance, separate from aqueous solution in crystals which contain no water and are said to be *anhydrous.*

When crystallized sodium carbonate is exposed to air it falls slowly to a white powder, which has the composition $Na_2CO_3.H_2O$, nine-tenths of the water being given off—

$$Na_2CO_310H_2O = Na_2CO_3.H_2O + 9H_2O.$$
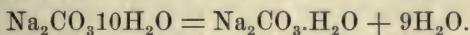
91. Efflorescence.—A substance which loses its water of crystallization in the air, falling to a powder in this way, is said to *effloresce.* This phenomenon, like deliquescence, depends on the quantity of water-vapor in the air. If transported to the Sahara, many crystallized salts which we call permanent would at once be classed as efflorescent. And in air saturated with water-vapor, $Na_2CO_310H_2O$, will not effloresce. It will *deliquesce,* absorbing water-vapor and producing a solution.

Mono-sodium carbonate, $NaHCO_3$, baking-soda, is a white crystalline powder. Its decomposition by heat into Na_2CO_3, water and carbon dioxide, has already been referred to. It is not used alone in the baking process because the sodium carbonate which would be left in the bread would make it nauseous and unwholesome. We place a little baking-soda in a beaker and pour some hydrochloric acid over it. A violent escape of carbon dioxide takes place:

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$
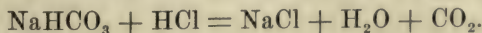
Thus, when an acid acts upon mono-sodium carbonate, the sodium salt of this acid—that is, a compound in which

the hydrogen which acids always contain is replaced by sodium—is produced, together with water, and carbon dioxide escapes.

92. **Baking-powder.**—A baking-powder is always a mixture of mono-sodium carbonate with some substance which acts upon it like an acid, liberating carbon dioxide from it. In the best powders, cream of tartar is employed for this purpose, while in cheaper powders alum is used.

93. *Sodium sulphate*, Na_2SO_4, is made by the action of sulphuric acid on salt—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$
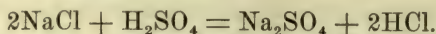
It separates from solution in water in large, colorless crystals of the composition $Na_2SO_4 10H_2O$, which effloresce in dry air. These crystals were formerly supposed to have wonderful medicinal qualities.

CHAPTER X

CHLORINE

94. Preparation.—Some coarsely powdered manganese dioxide is placed in a flask provided with a rubber cork in which are two perforations. Through one hole passes a tube having a funnel at the upper end; the lower end runs nearly to the bottom of the flask. The other hole carries a tube which runs just to the inside of the cork. This tube—called the delivery tube—is bent twice at right angles, and runs to the bottom of a large, empty jar. Chlorine gas, being about two and a half times as heavy as air, flows into the bottom of the jar like water and displaces the air, and this is the best way to collect it, for it is soluble in water and can not be collected over it.

Strong hydrochloric acid is poured through the funnel tube until about six times as much by weight has been introduced as of manganese dioxide. Then a small flame is placed under the flask, which has been supported on wire gauze to avoid cracking. The greenish-yellow color of chlorine rapidly appears in the generating flask, and then in the bottom of the collecting jar, from which it rises to the top. Then the tube is withdrawn, the ground-glass cover, which has been resting loosely on the jar, is tightly placed over it, the jar, which is now full of chlorine, is stood aside, and another takes its place. In this way a number of jars full of the gas can be collected, but great care must be taken not to inhale the gas, as it is very injurious. The apparatus employed is shown in Fig. 25.

Chlorine was first obtained in 1774 by the great Swedish chemist, Carl Wilhelm Scheele, who prepared it by the method just described. There are dozens of ways in which it can be made in the laboratory, but it happens that this same process is employed industrially for the production of the gas on a large scale.[1] Instead of glass flasks, large vessels of stoneware, or of flagstones bolted together, are used.

FIG. 25.—Preparation of chlorine from manganese dioxide and hydrochloric acid.

The chemical change which takes place in our flask is described by the equation:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$
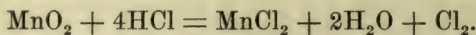
95. **Physical properties.**—Chlorine is a greenish-yellow gas, which has been converted by cold and pressure into a clear yellow liquid heavier than water. The gas is nearly 35.5 times as heavy as hydrogen, and therefore about $2\frac{1}{2}$ times as heavy as air. It has a suffocating smell, and its inhalation gives rise to dangerous inflammation of the mucous membranes of the respiratory passages, and may cause death. Even chlorine very much diluted with air is injuri-

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[1] At present this method of making chlorine on the large scale is being replaced by the electrolysis of solutions of potassium chloride, KCl, or of sodium chloride, NaCl. When the electric current is passed through such a liquid, chlorine is liberated at the positive pole.

ous, though experiments on dogs have shown that the quantity which can be borne without injury increases with habit. Water dissolves about twice its volume of the gas at ordinary temperatures. This solution is called chlorine water, and when it is cooled there separates from it in yellow scales a compound of chlorine with water of crystallization called chlorine hydrate, $Cl_2 8H_2O$. This separates again into chlorine and water, slowly, if kept in a freezing mixture, and rapidly at room temperature.

96. **Chemical properties.**—Chemically, chlorine is extremely energetic, easily entering into combination with many other elements; this is the reason it is not found as such in nature. When powdered arsenic is sprinkled into the gas it catches fire and burns to arsenic chloride, $AsCl_3$, a colorless poisonous liquid which floats in the jar for a time as a smoke. Powdered antimony behaves in the same way. A piece of phosphorus introduced into the gas in a spoon melts and then takes fire, burning with a pale flame to phosphorus trichloride, PCl_3, which then, if there is plenty of chlorine, combines with more of it, producing phosphorus pentachloride, PCl_5. Chlorine has no action upon carbon, and if a piece of glowing charcoal is plunged into the gas it is extinguished.[1] If a burning candle is plunged into chlorine the flame becomes red and feeble, and quantities of soot separate on the glass. The hydrogen of the candle burns in the chlorine to hydrochloric acid, HCl, but the carbon separates in the free state.

97. **Action of chlorine upon the metals.**—Chlorine acts upon the metals, converting them into chlorides, in many cases with evolution of light and heat. The brilliant combustion of sodium has already been described. Copper leaf

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[1] It must not be concluded from this that no compounds of chlorine with carbon are known. In most cases where two elements do not combine directly their compounds can be obtained by indirect methods, and it is so in the present instance.

—Dutch leaf, as it is called—takes fire, producing copper chloride. A brass wire, whose combustion can be started by placing a little Dutch leaf on the end, burns energetically, producing the chlorides of the metals of which brass consists—copper and zinc.

Some of these combustions are not interfered with by drying the chlorine, those of arsenic and antimony, for example. In other cases the action does not appear to occur at all when the gas is completely dry. Sodium and copper retain their luster in dry chlorine for years. In these cases, and in all other similar ones, it is probable that the presence of the water simply increases greatly the speed of a process which would occur, and yield the same products, in its absence. This, in fact, is what we mean by catalytic action. Copper, for example, combines with dry chlorine, but the change is so slow that it escapes detection: On addition of water-vapor the combination becomes very rapid, heat is evolved rapidly, the temperature rises high enough to make the products luminous, and we call the process a combustion.

98. **Combustion of hydrogen in chlorine.**—A hydrogen flame, fed by a generator containing zinc and dilute sulphuric acid, is lowered into a jar of chlorine. It continues to burn, but becomes large and pale. After a time the flame goes out, and then it is found that the chlorine has disappeared and the jar is filled with a colorless gas of quite different properties. This is hydrochloric acid, HCl. When equal volumes of hydrogen and chlorine are mixed in the dark and exposed to sunlight or to the light of burning magnesium, explosion takes place and hydrochloric acid is formed. If both gases are completely free from water no explosion occurs, nor does the mixture explode if kept very cold—at —12°, for instance. If the mixture is exposed to ordinary diffuse daylight, slow combination without explosion takes place.

99. **Action of chlorine upon hydrogen compounds.—
Bleaching.**—Chlorine even attacks hydrogen compounds,
removing some or all of the hydrogen to form hydrochloric
acid. In this way it slowly decomposes water in sunlight:

$$H_2O + Cl_2 = 2HCl + O.$$
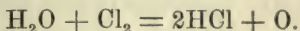
Upon these facts depends the bleaching action of chlo-
rine, for all vegetable and animal, and many artificial color-
ing matters, are compounds of hydrogen. Either the chlo-
rine attacks the coloring matter and destroys it by remov-
ing the hydrogen to produce hydrochloric acid, or else the
chlorine combines with the hydrogen of the water which is
always present in bleaching operations, and the oxygen lib-
erated destroys the coloring matter. Perfectly dry chlorine
does not bleach.

100. **Hydrochloric acid, HCl.**—A small, strong glass
tube, narrow at both ends and provided at each end with a
stop-cock, is covered with a wire-gauze jacket, to avoid dan-
ger to the eyes in case of breakage, and filled in the dark
with a mixture of equal parts of hydrogen and chlorine.
The tube employed is that shown in Fig. 29. The other
apparatus in the figure is not needed in this experiment.
The mixture is caused to explode by burning magnesium
wire near it. The tube now contains hydrochloric acid. It
is allowed to cool perfectly, one end is placed under the
surface of some mercury in a dish, and the stop-cock at that
end opened. No gas escapes and no mercury enters. This
shows that the volume of the hydrochloric acid produced
is equal to the sum of the volumes of the hydrogen and the
chlorine, or—

1 volume hydrogen + 1 volume chlorine = 2 volumes
hydrochloric acid.

101. **Combination of gases by volume.**—It is important
to notice the simplicity of these relations. It will be re-

called that we found a similar state of things in the combination of hydrogen and oxygen to steam:

2 volumes hydrogen + 1 volume oxygen = 2 volumes steam.

This is always the case when combination occurs between gases. There is always a *simple relation* between the volumes of the gases which combine. And if the compound is also a gas, there is also a simple relation between the volume of each gas and that of the compound. Precisely the same thing is true of decompositions in which gases are produced. This fact is usually called the *law of simple volume ratios.* It is true also of vapors.

102. Electrolysis of hydrochloric acid.—Our conclusion, that hydrochloric acid contains equal volumes of hydrogen and chlorine, can be corroborated by decomposing its aqueous solution by the electric current. For this purpose, the same apparatus can be employed which served in the electrolysis of water (Fig. 2). When the current passes, hydrogen separates at the negative pole and chlorine at the positive. It is necessary to allow the current to pass half an hour before measuring the gases. This is on account of the solubility of chlorine. Some of it dissolves at first, and the volume of the gas collected is smaller than that of the hydrogen, owing to this loss. Finally, the liquid becomes saturated with chlorine, no more of it dissolves, and the volume of gas collected at the positive pole is equal to that of the hydrogen at the negative.

103. Occurrence and preparation of hydrochloric acid.— Hydrochloric acid is contained in the gases which issue from volcanoes. Considerable quantities of it exist dissolved in the waters of several South American rivers, whose sources are in volcanic districts of the Andes. Industrially it is always obtained by the action of sulphuric acid, H_2SO_4, on salt. The operation is carried out in iron pans and the

reaction does not become complete until the mixture is heated nearly to redness:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$
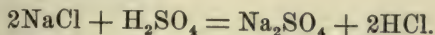
104. Preparation of hydrochloric acid gas in the laboratory.—For laboratory purposes it can be obtained from the same materials. But it is more convenient to start with the liquid hydrochloric acid of commerce. This is a solution of the gas, HCl, in water, made by passing it into cold water until the water will dissolve no more. Some of this liquid is placed in a flask with three necks. Through one passes the delivery tube, which conveys the gas to the jar in which it is to be collected. Another carries a dropping funnel, from which strong sulphuric acid is allowed to fall drop by drop (Fig. 26). We shall see later that sulphuric acid combines energetically with water. Each drop combines with a certain quantity of the water in the hydrochloric-acid solution, and the gas which was dissolved in this escapes. In this way an abundant supply of the gas can be obtained. When the stopcock of the funnel is turned so that sulphuric acid no longer enters the

Fig. 26.—Preparation of hydrochloric-acid gas.

flask, the current of gas ceases. The third neck carries a safety-tube, the bend of which contains a little mercury. This serves to prevent the pressure from rising too high in the bottle, for if so much gas is liberated that the delivery tube is unable to carry off all of it, the excess will escape through the safety-tube. The gas can not be collected over
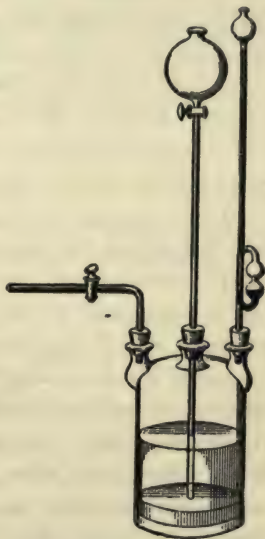
water on account of its great solubility. Small quantities can be collected over mercury, on which it has no action, and larger quantities by downward displacement in dry flasks.

105. Properties.—Hydrochloric acid is a colorless gas, with a pungent, irritating odor. By cold and pressure it has been converted into a colorless liquid, which has been frozen to a white crystalline solid. Water at 0° dissolves 500 times its bulk, and at ordinary temperatures about 400 times, and this solution is the hydrochloric, or " muriatic," acid of commerce. It is interesting to note, that while the quantity of the gas dissolved is increased by increasing the pressure, yet it is not proportional to the pressure, as we have seen to be the case with slightly soluble gases like oxygen. More gas will dissolve under two atmospheres than under one, but nothing like twice as much. All very soluble gases behave in this way.

The chemical behavior of hydrochloric acid can be summed up in the remark that it is a *strong acid*. The term " strong acid " has a very precise meaning in modern science, and we shall shortly inquire just what that meaning is. At present we can only remark that hydrochloric acid, like other strong acids, is energetic chemically, readily taking part in many chemical changes; but this energetic character is only shown when it is dissolved—practically we may say, when dissolved in water, for hydrochloric acid free from water is, whether gaseous or liquid, an inert substance.

106. Action upon the metals.—Into a beaker containing a little strong aqueous hydrochloric acid we throw a small fragment of sodium. The metal melts and runs about on the surface of the acid with a hissing noise. Hydrogen escapes and a mass of fine white crystals of salt falls through the liquid, thus:

$$HCl + Na = NaCl + H.$$
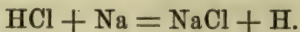
The aqueous acid acts similarly with many other metals. When we studied hydrogen we examined its behavior with zinc. We can now write the equation,

$$Zn + 2HCl = ZnCl_2 + H_2.$$
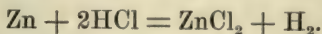
So with magnesium, there is energetic evolution of hydrogen—

$$Mg + 2HCl = MgCl_2 + H_2.$$
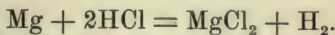
The chloride of the metal used is formed and hydrogen escapes. On the other hand, the water-free substance, liquid or gas, has no action upon zinc, magnesium, or sodium. Evidently the chlorides can be looked upon as hydrochloric acid in which the hydrogen has been removed and a metal inserted in its place. Thus, 23 parts of sodium replace 1 part of hydrogen, producing salt:

$$HCl, NaCl.$$
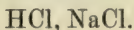
But 65 parts of zinc replace 2 parts of hydrogen, producing zinc chloride, in which the quantity Zn is combined with twice 35.5 parts of chlorine:

$$\left. \begin{array}{l} HCl, \\ HCl, \end{array} Zn \begin{array}{l} Cl, \\ Cl, \end{array} \right\} \text{ or } ZnCl_2.$$
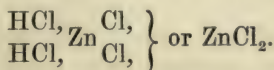
This relation between hydrochloric acid and the chlorides of the metals we express by calling the metallic chlorides the *salts* of hydrochloric acid. And, in general, a salt of an acid has the same composition as the acid itself, except that the hydrogen has been replaced by a metal.

There are some metals on which the action of hydrochloric acid is slight, silver, for instance; and others, like gold and platinum, on which it does not act at all.

107. Decomposition by heat.—Hydrochloric acid is a stable compound and is not at all separated into hydrogen and chlorine by a temperature of 1500°, which is far beyond a white heat. At 1800° it is partially decomposed.

7

108. **Preparation of the chlorides of the metals.**—Some metallic chlorides can be made in the same way as those of zinc, sodium, and magnesium by the action of aqueous hydrochloric acid upon the metal, hydrogen escaping. There are other methods of obtaining them. To a strong solution of sodium hydroxide in a beaker strong aqueous hydrochloric acid is added, drop by drop, with constant stirring. There is a violent reaction, much heat is evolved, and a mass of salt crystals separates:

$$NaOH + HCl = NaCl + H_2O.$$
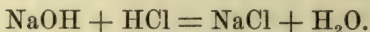
Some zinc oxide is covered with water and hydrochloric acid added, with stirring. The white powder disappears and a solution of zinc chloride, $ZnCl_2$, is produced:

$$ZnO + 2HCl = ZnCl_2 + H_2O.$$
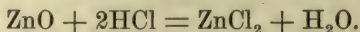
It is clear from the equations, that if the materials are pure no gas will be given off in either experiment, for the hydrogen does not escape. It forms water. The effervescence which usually occurs in the first experiment arises from sodium carbonate, Na_2CO_3, which is nearly always present as an impurity in the sodium hydroxide. We have remarked that this liberates carbon dioxide with hydrochloric acid:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$
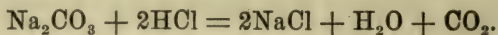
This leads us to another method of making metallic chlorides. The carbonate of a metal is treated with hydrochloric acid. Carbon dioxide escapes, water is formed, and the chloride in question dissolves and can be obtained by evaporating the liquid. This is the method usually employed in making calcium chloride, $CaCl_2$. Calcium carbonate, $CaCO_3$, which is called limestone, marble, or chalk, according to its condition, is dissolved in hydrochloric acid:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.[1]$$
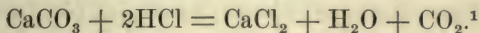
109. Insoluble chlorides.—The chlorides of the metals are mostly soluble in water. Silver chloride ($AgCl$), mercurous chloride (Hg_2Cl_2), and cuprous chloride (Cu_2Cl_2) are insoluble in it.[2] Lead chloride ($PbCl_2$) is slightly soluble in cold water, much more so when the water is hot. There are a few other insoluble and slightly soluble chlorides of less importance.

110. Chlorides of non-metallic elements.—The chlorides of non-metals like phosphorus and sulphur can not be obtained by the action of hydrochloric acid upon the element, for the acid does not act upon non-metallic elements in this way. Nor does it produce chlorides with the oxides or hydroxides of the non-metals. Only the metals form carbonates, so that the third method can not be applied. This leaves us only the direct action of chlorine upon the element, and it is in this way that the non-metallic chlorides

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[1] These three methods of making salts, by the action of the acid upon the oxide, the hydroxide, or the carbonate of the metal, apply not only to hydrochloric, but to most other acids as well.

[2] To call a substance insoluble is simply a short method of saying that its solubility is very small. Of course, instead of talking in this loose way, it would be better to measure the solubility of these substances and state the results in figures. A good beginning has been made in this direction. Silver chloride, for instance, is a typical "insoluble" substance, yet recently its solubility has not only been detected, but measured.

are usually prepared. We have seen the method applied in the case of phosphorus and arsenic. While the chlorides of the metals are usually soluble in water unchanged, those of the non-metals react chemically with it, producing hydrochloric acid and other products whose nature depends upon the chloride employed.

Compounds of Chlorine containing Oxygen

111. Three oxides of chlorine have been obtained:

Cl_2O, chlorine monoxide,
ClO_2, chlorine peroxide,
Cl_2O_7, chlorine heptoxide.

Chlorine monoxide, Cl_2O, is obtained by leading chlorine over cold mercuric oxide. The gas given off is condensed in a freezing mixture. It is yellowish-brown, with a peculiar odor, different from that of chlorine. By cooling it is converted into a dark-brown liquid. This can be distilled without decomposition if pure and if carefully heated, but the operation is not free from danger. Both the liquid and the gas explode violently on being heated quickly, and on contact with many substances—as, for instance, phosphorus and sulphur. This explosion is simply decomposition into chlorine and oxygen. Since the oxygen of chlorine monoxide is only loosely held, it tends to yield oxygen to any substance which can combine with that element. It violently oxidizes finely divided metals and many other substances, and this behavior is summed up in the statement that it is a strong oxidizing agent.

112. **Chlorine peroxide, ClO_2.**—A little strong sulphuric acid is placed in a small, strong glass cylinder, and 0.5 gram or less of finely powdered potassium chlorate introduced in small portions, the cylinder being covered with a card after each addition. Chlorine peroxide, a dark, greenish-yellow gas, rises and fills the cylinder. When it is very much

diluted with air, the odor of the gas is not unpleasant. The action of heat upon it is well shown by bringing into the upper part of the cylinder a glass rod which has been heated in the burner flame. Explosion instantly takes place, the gas being converted into chlorine and oxygen. Its behavior on contact with combustible substances can be illustrated by allowing a drop of ether to fall into another jar of the gas. There is an explosion. The ether is burned to carbon dioxide and water at the expense of the oxygen of the chlorine peroxide. Larger quantities of chlorine peroxide can be made by gently heating potassium chlorate with strong sulphuric acid in a flask, but the operation is dangerous. When led into a tube surrounded by a freezing mixture of ice and salt, the gas condenses to a red liquid, which, on more intense cooling, solidifies to a mass of yellow crystals.

113. *Chloric acid*, $HClO_3$, has never been obtained free from water. The strong solution is thick and colorless, and tends energetically to impart oxygen to oxidizable substances; paper wet with it catches fire after a time. Corresponding to chloric acid is a series of compounds in which its hydrogen is replaced by metals, e. g.:

$KClO_3$, potassium chlorate,
$NaClO_3$, sodium chlorate.
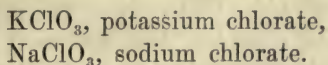
These compounds are called the *chlorates*.

114. **Potassium chlorate**, $KClO_3$, was the first to be discovered (1786), and is still the most important. It can be obtained by the action of chlorine on hot strong solution of potassium hydroxide:

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$
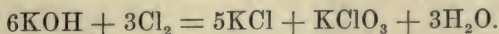
Since $\frac{5}{6}$ of the potassium present is wasted as potassium chloride in this reaction, the process is no longer used. Potassium chlorate is now made almost entirely by the action

of the electric current upon a solution containing potassium chloride, KCl, and potassium hydroxide, KOH. It would lead us too far to discuss the details of this interesting process here. The potassium chlorate separates out in crystals, which can be removed with a perforated ladle while fresh potassium chloride is added, so that the process is continuous. Potassium chlorate forms white anhydrous crystals, which are only slightly soluble in cold water, much more so in hot. Its solution is used in medicine as a gargle for inflamed mucous membranes of the throat. It is poisonous, and must not be swallowed.

The torpedoes which are placed on railway tracks as signals consist of small tin boxes, like blacking boxes, filled with a mixture of powdered sulphur and potassium chlorate; and we can understand their behavior by grinding a small crystal of potassium chlorate with a fragment of sulphur in a mortar. The sulphur is oxidized with explosion by the oxygen of the potassium chlorate. This illustrates the fact that mixtures of chlorates with oxidizable materials are explosive, and such mixtures have been used practically for blasting, but they are now abandoned, because they are sensitive to shock, and it is impossible to transport them safely.

Chlorine heptoxide, Cl_2O_7, is a colorless oil which is much more stable than the other oxides of chlorine. It explodes on being brought into a flame or when sharply struck, but it has no action on wood, paper, phosphorus, or other oxidizable materials.

115. Bleaching powder, $CaOCl_2$.—Some slaked lime, which is calcium hydroxide, $Ca(OH)_2$, is mixed to a paste with water, and poured into a flask filled with chlorine. Then the flask is closed with the hand and shaken vigorously. The color of the chlorine disappears, and the suction upon the hand—the flask will hang suspended from it—shows that the gas is being absorbed. When the absorption is complete we add a little nitric acid to the white substance in

the flask. The chlorine is again liberated, and soon fills the vessel.

Bleaching powder, or " chloride of lime," as it is called, is made in large stone chambers. On the floor a thin layer of slaked lime is placed and chlorine is passed in until the chamber is full of the gas. Then the chamber is closed and allowed to stand two or three days, after which the lime is raked up, exposing fresh surfaces, and the chlorine treatment repeated.

With respect to the chemical make-up of bleaching powder there has been much discussion. Most of the facts are fairly well summed up in the statement that it consists essentially of a compound $CaOCl_2$, which liberates its chlorine when treated with an acid—e. g.:

$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$
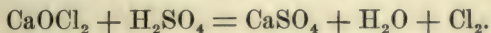
When well made it liberates 40 per cent or upward of chlorine in this way. It is simply a convenient way of preserving chlorine and shipping it, and all its uses depend upon the ease with which chlorine can be obtained from it. It is used as a disinfectant and, in enormous quantities, for bleaching.

CHAPTER XII

116. The subdivision of chalk.—Ordinary chalk is a white, odorless, tasteless, brittle solid. If a piece of it is broken in two, each portion remains chalk as before—there is no alteration in properties as a result of the division. Instead of breaking the chalk with the fingers, it will be easier to put it in a mortar and grind it. In this way we can pulverize chalk very finely, but we soon reach the limit of the process—the powder packs together in the bottom of the mortar, and further grinding is useless. If, now, we examine some of this powder under a microscope, it becomes clear that every grain of it is simply a little mass of chalk, which possesses a definite shape and has, in general, all the properties which we commonly associate with that substance.

Here we are at the end of our resources. So far as we know *practically,* chalk remains chalk no matter how fine the grains of the powder become.

Now let us take another, a very important, step. Let us carry forward the division of the chalk *in thought.* We can pick out a grain of the powder and imagine a plane passed through it so as to divide it into two equal parts. Then repeat this operation with each half, and so on. Clearly this is purely a mental process, and the results we get from it will be ideas, not facts.

At once we are face to face with two possibilities, both of which are as old as human knowledge itself:

First. The subdivision of the chalk can be carried out without limit. No matter how small a mass of chalk we think of, it can still be subdivided into two smaller masses. This view, when applied not only to chalk but to all matter, is called the *doctrine of the infinite divisibility of matter*.

Second. Ultimately we should reach a particle of chalk so small that if a plane were passed through it, different kinds of matter would lie on the two sides of the plane. The chalk would cease to be chalk when this subdivision was made, and would yield two new substances. This view is the opposite of the preceding one. It may be called the doctrine that matter is not infinitely divisible, or, more shortly, *the atomic theory*.

So far as the subdivision of chalk is concerned, we are not forced to choose between these alternatives. We might answer that, not being able to carry out the process, we do not know whether chalk is infinitely divisible or not. Nevertheless, for practical reasons, it is necessary to make a choice. *It has been found that the second view, the atomic theory, aids us immensely in remembering and classifying physical and chemical facts, while the first is nearly worthless in these respects.*

117. **Molecules.**—The smallest mass of chalk which we can think of—that mass which ceases to be chalk and becomes something else when we divide it further—we shall call a *molecule* of chalk. Any mass of chalk consists of molecules, all of which are alike. So does any other pure substance, but the molecules of two different substances are different. These molecules are not to be thought of as being in contact; there are spaces between them, and, if we like, we may think of these spaces as filled with the *ether* of physics, though this assumption does not help us much in dealing with chemical facts.

118. **Movement of the molecules in solids, liquids, and gases.**—In a solid, a molecule moves constantly, but, on the

whole, remains in about the same locality, the motion being like that of the earth around the sun or of a vibrating tuning-fork. In a liquid or a gas, a molecule moves in a straight line until it strikes another molecule or the wall of the containing vessel, the motion being like that of a swarm of bees enclosed in a box. When one of these encounters occurs the molecule does not ordinarily return to the same place, but rebounds in some new direction. The great difference between liquids and gases is, that in a liquid the molecules are crowded together, and each one only travels a very short distance before it strikes another; in a gas, the crowding is not so great, and the free path of a molecule—the distance it travels before an encounter takes place—is longer.

These distinctions are only rough. Many facts—for instance, the traveling of gold into lead (p. 19)—show that, under some circumstances, molecules of solids must be assumed to desert their original position and move forward to a new one some distance away, and molecules continually leave the surface of all liquids and many solids and begin to play the *rôle* of gaseous molecules in the surrounding space. This occurrence is *evaporation*, and the molecular motion of solids, liquids, and gases is *heat*.

119. **Size of the molecules.**—Some physical facts are best dealt with by giving a definite size to the molecule. According to these facts, about 5,000,000 molecules laid side by side in contact would make a line one centimeter long. This corresponds to about 12,500,000 of them in an inch. In this calculation it is assumed that the molecules are spheres. This shape the chemist can not give to the molecules by means of which he describes chemical phenomena, because his facts will not allow him to do so.

At present, chemical facts do not force us to assign any size to the molecules. It is sufficient to think of them as

very minute—so small that the smallest visible fragment of any substance must be thought of as containing many millions.

120. **Atoms.**—It has been said that, from the standpoint of the atomic idea, any mass of chalk is to be thought of as consisting of molecules, all of which are exactly alike. Let us now place some chalk in a vessel which will stand a very high temperature—a platinum vessel is best—and heat it to whiteness, arranging the apparatus in such a way that any gas given off can be collected over mercury. A colorless gas collects over the mercury, which can be shown to be *carbon dioxide*, CO_2. When the operation is over, we open the platinum vessel and find in it common lime, which is *calcium oxide*, CaO.

Now, since every molecule of chalk is like every other, each one must have separated into at least one molecule of lime and one of carbon dioxide. By methods which we need not discuss, lime can be proved to contain calcium and oxygen and carbon dioxide to contain carbon and oxygen, and it is clear that each molecule of chalk must be thought of as containing these three constituents.

Hence the necessity for thinking of the molecule, not as a simple mass, but as a structure built up of smaller masses, the ATOMS. We must think of each molecule of chalk as containing at least four atoms, one of calcium, one of carbon, and two of oxygen, one of which goes with the calcium atom and the other with the carbon atom when the molecule is broken up by heat. By further reasoning it can be shown to contain five atoms, for the molecule of carbon dioxide contains two atoms of oxygen, both of which must have come from the chalk, and therefore there must be three oxygen atoms present, not two.

Atoms, then, are the smaller particles of which molecules consist. The atoms of the same element are all exactly alike; every atom of hydrogen is like every other

atom of hydrogen; every oxygen atom is like every other. When we say that the atomic weight of oxygen is 16, then, if we happen to be thinking of molecules and atoms and not of matter in visible masses, what we mean is this: *that the oxygen atom weighs 16 times as much as the hydrogen atom. It makes no difference what the weight of the hydrogen atom is. That does not interest us in the least. We are concerned only with the statement that, whatever the weight of the hydrogen atom may be, that of the oxygen atom is 16 times as great.*

Since all hydrogen atoms are alike and all oxygen atoms are alike, this is a perfectly definite statement, and is true of all pure hydrogen and oxygen without regard to the source or the method of preparation.

121. The chemical laws from the standpoint of atoms and molecules.—It will now interest us to go over the chemical laws, which we have previously studied simply as facts, and to see what appearance they present when we make use of the ideas of molecule and atom in stating them. In doing this we are not bringing forward anything new. We are simply stating the same old facts in a new language—the language of the atomic theory.

122. The law of the indestructibility of matter.—In the first place, the atoms are not destroyed and are not created in chemical operations, they simply continue to exist. As John Dalton, the founder of the atomic theory in its present form, remarked in 1808: "We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen." Hence the *law of the indestructibility of matter.* Each atom is conceived as indestructible, and, since all matter consists of atoms, no destruction is possible. After any chemical change the number of atoms remains the same as before it.

On the other hand, the total number of *molecules* can

be very greatly altered by chemical changes. We have just discussed the decomposition of chalk by heat. The equation for this decomposition is—

$$CaCO_3 = CaO + CO_2,$$

and if we consider that each symbol means an atom of the corresponding element and each formula a molecule of the compound, we perceive that every molecule of chalk yields two molecules, one of lime and one of carbon dioxide, so that the total number of molecules present is doubled. But the number of atoms remains five as before.

123. **The law of definite proportions.**—Similarly with the *law of definite proportions.* The formula of hydrochloric acid is HCl, and we have thought of this as meaning one atomic weight of hydrogen, weighing 1 (1 gram, for instance), and one atomic weight of chlorine, weighing 35.5 (35.5 grams). But we are at liberty to think of any unit of weight we please. Let us make our unit of weight the *hydrogen atom.* Then the formula HCl means an atom of hydrogen, weighing 1, in union with an atom of chlorine, weighing 35.5 times as much. These together form a molecule of hydrochloric acid, which must weigh 36.5 times as much as the hydrogen atom.

Both these atoms possess an invariable weight, and therefore the composition of a molecule of hydrochloric acid must be always the same. It must contain $\frac{1}{36.5}$ of its weight of hydrogen and $\frac{35.5}{36.5}$ of chlorine. But any mass of hydrochloric acid consists simply of a great number of such molecules, and its composition must be the same as that of a single molecule. Accordingly, the composition of hydrochloric acid must be constant. The same reasoning applies to all compounds.

124. **The law that it is impossible to transform one element into another.**—Since an atom simply continues to exist and can not be converted into any other atom, the

atomic theory gives us a clear picture of the fact that one element is never transformed into another.

125. The atomic weights.—We have seen that there is for each element a natural quantity by weight in which it enters into its compounds. According to the atomic theory, these numbers are simply the relative weights of the atoms, that of the hydrogen atom being 1. The molecule of hydrochloric acid contains two atoms, one of hydrogen and one of chlorine, and the chlorine atom weighs 35.5 times as much as the hydrogen atom. Every compound of chlorine consists of molecules which contain chlorine atoms in union with those of other elements. Thus, every compound of chlorine must contain 35.5 parts of chlorine by weight or— if it contains more than one atom of chlorine—some multiple of that quantity.

126. The law of multiple proportions.—The two compounds of hydrogen and oxygen, water (H_2O), and hydrogen peroxide (H_2O_2), have been described. Starting with water, let us admit that there is a second compound of the same two elements, richer in oxygen but containing the same two atoms of hydrogen in the molecule. Then it is clear that this second compound must contain at least two atoms of oxygen, and have the formula H_2O_2, for we can not divide the oxygen atom, and any compound between the two is impossible. Still increasing the oxygen, the next possibility would be H_2O_3 and the next H_2O_4, and there are indications that these compounds exist, though they have not yet been obtained.

Statements precisely like this can be made for every case where the same two elements form more than one compound. In every such case, if we suppose the quantity of one element to remain the same, the quantity of the other element will increase by a leap, so that its quantity in the second compound is double or triple or some small multiple of that in the first. Intermediate compounds do

not exist. This fact is commonly called the *law of multiple proportions*. As we have just seen, our atomic theory gives us a simple account of it. For, if we suppose the quantity of the second element to increase at all, it must increase by at least one atom in the molecule. And since the atoms are not divided, no compound between can exist.

law of multiple proportions —
When any two elements A & B combine
to form more than one compound
amounts of B which unite with a
amount of A bear the ratio of sma
whole numbers to each other.

CHAPTER XIII

THE ATMOSPHERE—NITROGEN

127. **Historical.**—Aristotle, whose views were accepted without question through the middle ages, considered the air to be an element. During the seventeenth century Boyle opposed this idea, and announced that it was probably a complicated mixture. This opinion rapidly gained ground during the hundred years that followed, but it was not supported by convincing experiments until near the close of the eighteenth century (1772). We already know that when a candle is burned, the products are the gas carbon dioxide and the vapor of water. If the candle is placed in a closed vessel, it will go out when the oxygen is all, or nearly all, converted into these two substances. Then, when the vessel cools, the water-vapor will condense on its walls and the gas in it is a mixture of carbon dioxide with air from which the oxygen has been removed, for the other constituents are not affected by the combustion. The next step is to get rid of the carbon dioxide, and this is easily accomplished by introducing a little lime, which greedily absorbs it. Daniel Rutherford, an English physician, carried out this experiment in 1772, and it is clear that it amounts to simply subtracting the oxygen from the air. He found the residual gas to be colorless and odorless. It extinguished burning substances and he named it *mephitic air,* because it instantly suffocated a mouse placed in it. By allowing a mouse to suffocate in a sealed vessel full of air, and then absorbing the carbon dioxide which its lungs had produced by lime, he
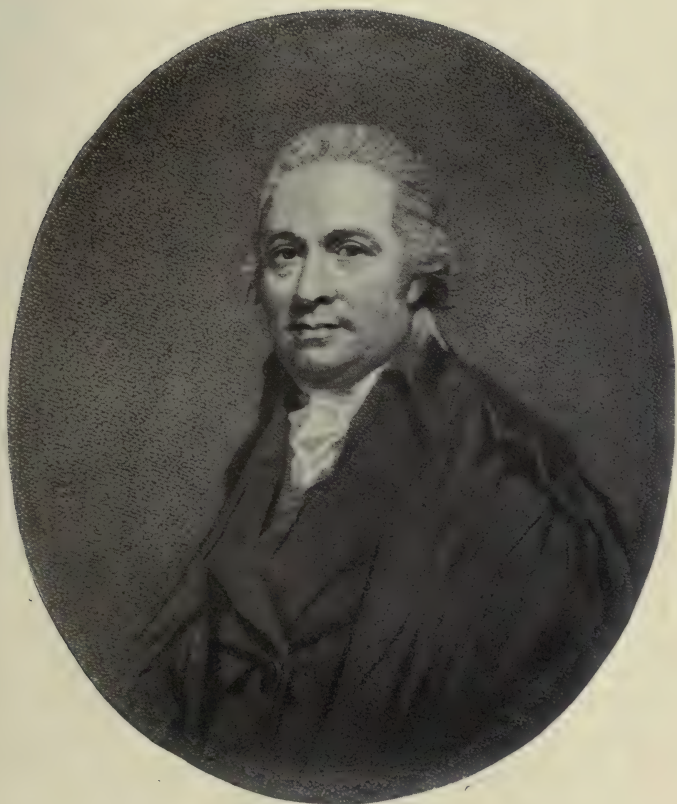
DANIEL RUTHERFORD

B. Edinburgh, 1749. D. 1819.

obtained the same gas. At the time, and for more than a century afterward, it was considered an element and named *nitrogen*. Within the last few years it has been found that, while the gas obtained by removing the oxygen from air does consist very largely of nitrogen, it also contains small quantities of argon and other elements recently discovered.

128. Composition of the atmosphere.—The air consists mainly of the two gases, nitrogen and oxygen, and if everything else were removed from it it would contain by volume—

Nitrogen, 79 per cent;
Oxygen, 21 per cent;

by weight—

Nitrogen, 77 per cent;
Oxygen, 23 per cent.

129. The air is a mixture, not a compound.—These gases are not chemically united, they are simply mixed. Perhaps the strongest proof of this statement is the fact that the percentage of oxygen in the air, even in pure open air of the country or seashore, varies. Sometimes it falls as low as 20.8 per cent, while in the air of mines and crowded rooms it may drop to 20.2 per cent. If the air were a compound, the proportion of oxygen in it would be always the same.

130. Analysis of air.—There are various ways of analyzing the air. One is to pass air—which must be carefully purified beforehand—through a weighed tube containing red-hot copper. This absorbs the oxygen, producing black cupric oxide (CuO). The increase in weight of this tube is the quantity of oxygen. The rest of the air (nitrogen mainly, but containing also argon and traces of other elements) passes into a glass globe which has been previously exhausted at an air-pump and weighed. The increase in weight of the globe gives the quantity of nitrogen with

8

argon and the other elements which are present only in small quantities.

131. Solubility of air in water.—Both nitrogen and oxygen dissolve in water, and when we expel air from water by boiling and analyze it, we find that it contains 35 per cent of oxygen, considerably more than ordinary air. This difference is very important to marine life. At the same time it furnishes an interesting proof that the air is a mixture, for if it were a compound the composition of the dissolved air would be the same as that of the original air.

132. Other constituents of the air.—The nitrogen obtained by removing oxygen from air contains a little more than 1 per cent by volume of *argon,* and small quantities of four other elements—*helium, krypton, neon,* and *xenon*— about which little is known at present, but which appear to resemble argon closely. All these elements are colorless gases. The most interesting peculiarity of argon, and probably of the others, is its complete inertness chemically.[1] All attempts to induce it to take part in chemical changes have failed, and it appears that we have here the first example of an element altogether destitute of chemical activity, a new form of matter.

Water-vapor is always present in the air, the quantity being very different at different times. It is called "humidity" in the weather reports, and much of it makes a moderately warm day very oppressive because it interferes with the evaporation from the body. The air contains about

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[1] Helium is just as inert as argon; the others have not yet been investigated in this respect. Helium is the only gas which has thus far resisted all attempts to liquefy it. It has been strongly compressed and cooled to −260° by means of boiling liquid hydrogen without liquefaction. If the helium is then allowed to expand suddenly, a further fall of temperature to −264° occurs, and the gas appears misty from incipient condensation, but no visible liquid is produced.

3 parts in 10,000 by volume of *carbon dioxide* (CO_2). The quantity varies but little; it rises slightly in winter in the temperate zone, because plant life is mostly at a standstill and combustion and respiration are more active. On this small percentage of carbon dioxide the existence of the whole vegetable world, and through it of animals also, depends. Recently the existence of a little hydrogen (2 parts in 10,000) has been announced. There are present also traces of ammonia (NH_3) and nitric acid (HNO_3), which are washed down into the soil by rains and furnish an important source of nitrogen to plants.

Nitrogen, N = 14

133. The discovery of nitrogen and its occurrence in the air have already been discussed. It is not an important constituent of the earth's crust. The chief compounds of the element which occur in nature are potassium nitrate, KNO_3, commonly called saltpeter, and sodium nitrate, $NaNO_3$, and these are found only in small quantities except in some special localities.

134. **Preparation.**—It is easy to remove the oxygen from air, and the gas which remains—although, as we have seen, it still contains argon and several other elements—behaves like pure nitrogen in most respects. We can pass air through a tube containing red-hot copper, which will retain the oxygen in the form of cupric oxide. The nitrogen

Fig. 27.—Analysis of air by means of phosphorus.

passes on unchanged, and can be collected over water. Or a graduated tube full of air and sealed at one end is placed

with the open end in water, and a piece of phosphorus thrust up into the air on a wire (Fig. 27). Phosphorus combines slowly with oxygen at ordinary temperatures, and in the course of several days it will completely remove the oxygen of the air in the tube. This gradual absorption is shown by a gradual rise of the water into the tube. About one-fifth of the air is absorbed. Then the level of the water remains constant because nitrogen and the other elements are not acted upon by phosphorus.

In order to obtain nitrogen free from argon we must resort to chemical methods of making it. One way is to pass chlorine into an aqueous solution of the compound of nitrogen and hydrogen—ammonia, NH_3. The chlorine robs the ammonia of its hydrogen, liberating free nitrogen:

$$NH_3 + 3Cl = 3HCl + N.$$
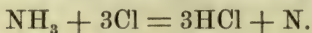
The hydrochloric acid does not remain free. It unites with more ammonia, producing ammonium chloride, NH_4Cl:

$$NH_3 + HCl = NH_4Cl,$$
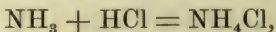
so that the final results are the liberation of nitrogen as gas and the production of ammonium chloride in the liquid. This experiment must be carried out with care, for if we pass in too much chlorine there is produced nitrogen chloride, NCl_3, a dangerously explosive substance.

A better method is to heat a white solid called ammonium nitrite, which has the composition NH_4NO_2. On gentle heating it separates into water and nitrogen:

$$NH_4NO_2 = 2H_2O + N_2.$$
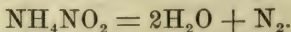
It is somewhat difficult to obtain ammonium nitrite pure, and for this purpose quite unnecessary. Practically, we use a mixture of sodium nitrite, $NaNO_2$, with ammonium chloride, NH_4Cl. The first thing that happens is the production of ammonium nitrite:

$$NaNO_2 + NH_4Cl = NH_4NO_2 + NaCl.$$
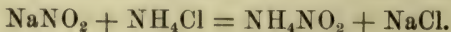
This then decomposes:

$$NH_4NO_2 = 2H_2O + N_2.$$
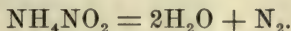
The mixture is placed, with enough water to form a thin paste, in a small flask provided with a delivery tube, and carefully heated. The nitrogen is collected over water (Fig. 28).

135. **Physical properties.**—Nitrogen is a colorless, odorless gas. Its solubility in water is very slight, 100 volumes of the latter dissolving less than $1\frac{1}{2}$ volumes of the gas at ordinary temperatures. From this we should expect it to be difficult to liquefy, and this is the case; yet by pressure and cold together it has been converted into a colorless liquid. When liquid nitrogen evaporates it absorbs heat rapidly from surrounding objects, producing intense cold; and if the evaporation is made more rapid by placing the vessel under an air-pump, the temperature falls to —225° and the nitrogen freezes to a snow-like mass. This was for a long time the greatest cold attainable, but recently temperatures more than 30 degrees lower have been obtained by the evaporation of liquid hydrogen.

Fig. 28.—Preparation of nitrogen from ammonium nitrite.

Since the air is nearly four-fifths nitrogen by volume, it is hardly necessary to remark that the gas is not poisonous. On the other hand, it is clear that an animal placed in it must immediately die by suffocation, which is only another name for lack of oxygen.

136. **Chemical properties.**—Chemically, nitrogen is inert at ordinary temperatures. Burning substances—a candle, phosphorus, and charcoal, for instance—plunged in it are extinguished at once. At higher temperatures it is

more energetic, and combines directly with many other elements—e. g., boron, lithium, and magnesium—producing with them compounds called nitrides; for example, magnesium nitride, Mg_3N_2. When a stream of electric sparks is passed through a mixture of nitrogen and oxygen—air will

answer every purpose—the two combine, producing the red gas nitrogen peroxide, NO_2 (Fig. 29). Under somewhat similar conditions—continual supply of energy in the form of electricity—nitrogen can even be made to burn in air with a flame which is hot enough to melt a platinum wire. When the air is intensely heated in any way—for instance, by burning mag-
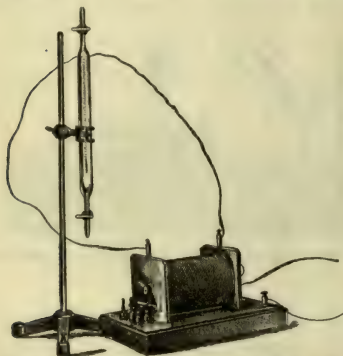
FIG. 29.—Combination of nitrogen and oxygen under the influence of a stream of electric sparks.

nesium in it—the nitrogen and oxygen combine to a very perceptible extent, and the same red gas is produced.

137. **Relation of nitrogen to life.**—Nitrogen is an important element in organic nature. All forms of life, animal or vegetable, contain a large proportion of it, and the same may be said of carbon, hydrogen, and oxygen. These four are preëminently the organic elements. However, many other elements are essential constituents in living matter, but are present in smaller quantities.

When animal matter decays, the nitrogen is mostly converted into ammonia, NH_3. About one tenth of the nitrogen escapes in the free state. The ammonia is washed into the soil by rains, absorbed by plants, and converted into complex nitrogenous compounds which serve as food for animals. Some plants, like peas, beans, and clover, absorb the free nitrogen of the air and convert it into complex compounds. Such plants have little nodules upon their roots, composed of certain species of bacteria.

CHAPTER XIV

COMPOUNDS OF NITROGEN AND HYDROGEN

138. Ammonia, NH$_3$.—This gas is a product of the decay of organic matter, and in this way gets into the atmosphere, which usually contains a trace of it. It finds its way also into natural waters, and the presence of ammonia indicates that a water is unfit to drink, for it is evidence of recent contamination with organic matter, probably sewage.

139. Combination of nitrogen and hydrogen.—When a mixture of nitrogen and hydrogen is confined in a tube over mercury and a series of electric sparks passed through it, the level of the mercury rises and partial union of the two to form ammonia takes place. The apparatus used is that shown in Fig. 4.

140. Chemical equilibrium.—The combination is never complete. On the contrary, if we confine *ammonia gas* over mercury and treat it with electric sparks in the same way, the level of the mercury falls and a partial *separation* into nitrogen and hydrogen occurs. It makes no difference whether we start with ammonia or with the mixture of nitrogen and hydrogen, the final state of things will be the same. In both cases the gas in the tube will contain the same percentages of hydrogen, nitrogen, and ammonia when the process is over. We may consider that two processes occur together in both experiments—the union of the nitrogen and hydrogen to ammonia, and the separation of the ammonia into its constituents. Whether there is observed, on the whole, separation or union, will depend on whether the reaction,

$$N + 3H = NH_3, \text{ or}$$
$$NH_3 = N + 3H,$$
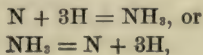
occurs more rapidly. When the two have the same speed—that is, when just as much ammonia is decomposed in a second as is produced in the same time there is *equilibrium*—the process is stationary. Many chemical changes behave in this way.

141. Source of the ammonia of commerce.—Bituminous coal always contains a little nitrogen, and when it is distilled for the production of illuminating gas, the nitrogen unites with some of the hydrogen which such coal always contains, producing ammonia. This is finally obtained in a very impure form in solution in water, and this liquid, called gas liquor, is the source of nearly all the ammonia of commerce.

142. Preparation of ammonia gas in the laboratory.—The most convenient way of obtaining ammonia gas in the laboratory is to heat ordinary "ammonia water," which is the aqueous solution of the gas. The ammonia water is placed in a flask with a delivery tube and heated gently (Fig. 30). The gas
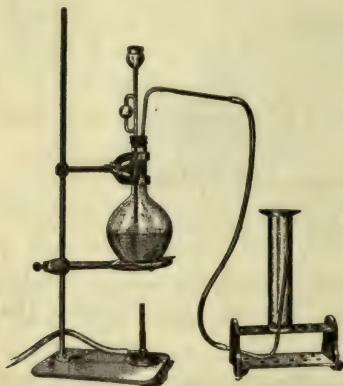
FIG. 30.—Preparation of ammonia gas from ammonia water.

can not be collected over water, for it is very soluble in that liquid. For this reason, so long as water was the only liquid used by chemists in collecting gases, ammonia remained undiscovered; and when, in 1774, Priestley used mercury in place of the water, its discovery was one of the first results of the new method. On account of its great weight, mercury can not well be used for collecting large quantities, and there is nothing left but the method of dry displacement, which we have already employed in the case of chlorine. But ammonia is much lighter than air. Hence we

invert the jar in which we wish to collect it, and pass the tube conveying the gas up to the bottom of the jar. The displaced air flows out around the mouth of the jar.

143. Properties.—Ammonia is a colorless gas, with a sharp, peculiar odor. It is not poisonous, but its action on the mucous membrane is irritating, and the prolonged breathing of air containing small quantities is attended with bad results. It is easily converted by cold or pressure, or by both together, into a colorless liquid. This liquid produces great cold when it evaporates, and is largely employed for cooling and for the production of artificial ice, for which purpose it has almost completely displaced other substances in practical work.

144. Combustion of ammonia in air and oxygen.—Ammonia will not burn with a continuous flame in the air. If a tube through which the gas is issuing is held near a lighted burner, the ammonia burns around the gas flame as a pale yellow mantle, but is extinguished when the Bunsen flame is removed. In oxygen, on the contrary, it burns steadily with a peculiar yellow flame. The hydrogen burns to water and the nitrogen is liberated:

$$2NH_3 + 3O = N_2 + 3H_2O.$$
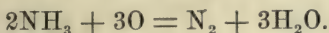
Ammonia is one of the very soluble gases. One volume of water absorbs at 0°, and under the pressure of one atmosphere over 1,100 volumes of it. Ammonia water, or "hartshorn," is an aqueous solution of the gas. This solution is colorless and has the odor of the gas. When swallowed, it acts as a powerful irritant poison. It is largely used in the laboratory and in the household.

145. Ammonium compounds.—A cylinder is filled with ammonia and another similar one with hydrochloric acid. Both are covered with glass plates. The cylinders are brought mouth to mouth and the plates removed, so that

the gases mix. At once a dense white smoke fills the interior of both vessels, and in a little while deposits as a white film on the glass (Fig. 31). This is ammonium chloride, NH_4Cl, produced by combination:
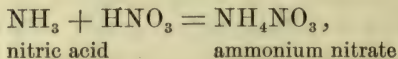
$$NH_3 + HCl = NH_4Cl.$$

FIG. 31.—Combination of ammonia gas with hydrochloric-acid gas.
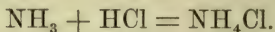
It is worth noting that, if both gases are *completely* free from water, they will remain clear when mixed, no ammonium chloride being produced. The presence of the smallest trace of water-vapor gives rise at once to the combination in which it takes no part. This is a remarkable case of catalytic action.

Ammonia combines with other acids, producing compounds in which the hydrogen of the acid is replaced by the group NH_4, and which are called *ammonium salts*—

$$NH_3 + HNO_3 = NH_4NO_3,$$
nitric acid   ammonium nitrate

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4,$$
sulphuric acid   ammonium sulphate
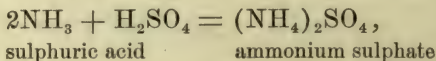
and so on. These salts are white, unless the acid combined with the ammonia is colored; and are soluble in water. When heated many of them are completely converted into vapor, leaving no residue, and this vapor is usually not that of the unchanged salt, but a mixture of ammonia and the acid. Thus, when ammonium chloride is heated, it disappears completely, and the vapor is a mixture of ammonia and hydrochloric acid in equal volumes:

$$NH_4Cl = NH_3 + HCl.$$
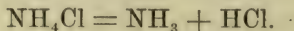
If the ammonium chloride is *absolutely* dry it is converted into vapor without this separation.

Every acid yields its corresponding ammonium salt, but the three whose formulas have been given are the most important. *Ammonium chloride* has a healing action on inflamed mucous membranes, and is a frequent ingredient in cough mixtures and lozenges. *Ammonium sulphate* is placed on the soil as a source of nitrogen to crops, and is used extensively in the manufacture of alum. *Ammonium nitrate* is employed in the manufacture of nitrous oxide gas, so much used by dentists. All three are white and crystalline, and readily soluble in water.

146. **Radicals.**—We have learned to regard the formula NaCl as meaning a compound containing 23 parts of sodium and 35.5 parts of chlorine by weight. We can now think of it also as meaning a molecule containing an atom of chlorine weighing 35.5 and one of sodium weighing 23. Now, the compound NH_4Cl is also a chloride, but instead of containing a single atom like Na united with the Cl, it contains a group of atoms consisting of one nitrogen and four hydrogen atoms, a group which we indicate therefore by the formula NH_4. This group, which is able to fill the place of the sodium, and to form a chloride in which it exists in union with Cl, just like an element, is called *ammonium,* and the term *radical* is applied as a class name to all such groups. Thus, ammonium, NH_4, is a *radical,* and all the compounds in which we assume it to exist are called ammonium compounds, just as compounds containing Na are called sodium compounds. Many such compounds are known, e. g.:

Ammonium compounds.	Sodium compounds.
NH_4Cl (ammonium chloride)	NaCl.
NH_4OH (ammonium hydroxide)	NaOH.
NH_4Br (ammonium bromide)	NaBr.
$(NH_4)_2CO_3$ (ammonium carbonate)	Na_2CO_3.
NH_4NO_3 (ammonium nitrate)	$NaNO_3$.

Notice, that in this list—and it might be much extended —the likeness between the ammonium and sodium com-

pounds is complete, provided we assume that NH_4, one atom of nitrogen and four of hydrogen, plays the same *rôle* in the molecule as Na, one atom of sodium, in the molecule of the corresponding sodium compound.

Many other radicals are known. We have noticed that sodium hydroxide, NaOH, and ammonium hydroxide, NH_4OH, both contain the complex OH. All hydroxides contain it, for example:

<div style="text-align:center">

Lithium hydroxide, LiOH;

Potassium hydroxide, KOH;

Calcium hydroxide, $Ca(OH)_2$.

</div>

OH is therefore a radical, and is called *hydroxyl*.

147. *Ammonium hydroxide*, NH_4OH, is produced in small quantities, when ammonia, NH_3, dissolves in water:

$$NH_3 + H_2O = NH_4OH.$$
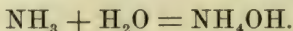
It is very unstable, and has never been obtained in the solid state.

In addition to ammonia, two other compounds of hydrogen and nitrogen have been prepared.

Hydrazine, N_2H_4, is a colorless liquid with an ammoniacal odor. When heated it boils, passing into a colorless vapor. Like ammonia, it combines with acids.

Hydrazoic acid, N_3H, is a colorless gas with a penetrating, intolerable odor. It is very soluble in water, and the solution is strongly acid, dissolving many of the metals—zinc and iron, for instance—with evolution of hydrogen.

CHAPTER XV

COMPOUNDS CONTAINING NITROGEN AND OXYGEN

14'8. Four *oxides of nitrogen* are known:

> Nitrous oxide, N_2O;
> Nitric oxide, NO;
> Nitrogen peroxide, $NO_2(N_2O_4)$;
> Nitrogen pentoxide, N_2O_5.

Another compound, N_2O_3—nitrogen trioxide—is often described, but its existence is doubtful.

149. **Nitrous oxide,** N_2O, is made by gently heating ammonium nitrate in a glass flask:

$$NH_4NO_3 = N_2O + 2H_2O.$$
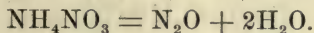
The gas can be collected over water, though some of it will dissolve and be lost.

Nitrous oxide is a colorless gas, with a slight pleasant odor and a faint sweet taste. Water dissolves a little more than its own volume under ordinary temperature and pressure. The gas is readily converted by cold or pressure into a colorless liquid. This liquid is made in large quantities, and is sold in strong steel cylinders for the use of dentists. When nitrous oxide is inhaled brief insensibility results, and this fact is utilized in the extraction of teeth.

Nitrous oxide is decomposed into its elements by heat. This fact is the key to its peculiar behavior toward combustible substances. An instructive experiment in this connection is to place a piece of phosphorus in nitrous oxide

111

and touch it with a hot metallic rod. The phosphorus melts and vaporizes at the point touched, but does not catch fire because there is no free oxygen present. But if the phosphorus is placed in air and its combustion started and then plunged into the gas, it burns brilliantly, because the heat of the flame separates the nitrous oxide into its elements, and the free oxygen supports the combustion. Sulphur feebly burning is extinguished when placed in nitrous oxide, but if the sulphur is burning vigorously its combustion continues.

150. **Nitric oxide**, NO, is made by means of the same apparatus which we employed in making hydrogen (Fig. 10). Copper turnings covered with water are placed in the gas bottle and nitric acid gradually added through the funnel tube. The gas in the bottle is reddish brown at the start because the NO which is liberated at first combines with the oxygen of the air and produces the strongly colored gas NO_2. Soon this is swept out and the gas becomes colorless. This is nitric oxide. It can be collected over water, in which it is almost insoluble. The equation is:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$
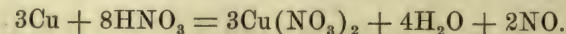
Nitric oxide is a colorless gas which can be converted by pressure and cold into a colorless liquid. Its odor is unknown because, as soon as it comes in contact with air, it combines with more oxygen and produces the strongly smelling gas NO_2. For the same reason we know nothing regarding its action on the body. It is impossible to inhale it, for it would come into contact with free oxygen in the lungs, and there produce NO_2, which is violently poisonous. In order to avoid this, Sir Humphry Davy filled his lungs first with nitrous oxide and then inhaled nitric oxide. The result was a burning sensation in the throat so intense that the experiment was discontinued.

So far as supporting combustion is concerned, the be-

havior of nitric oxide is somewhat the same as that of nitrous oxide, but a higher temperature is required to separate it into its constituents, and it extinguishes some combustibles, like sulphur and a candle, which will continue to burn in nitrous oxide. Yet a substance which will burn in it—phosphorus or magnesium, for instance—burns more brilliantly than in nitrous oxide because it is more liberally supplied with oxygen. The equations—

$$2N_2O = 2N_2 + O_2,$$
$$2NO = N_2 + O_2$$
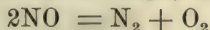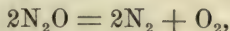
show that in the decomposition of nitrous oxide the mixture produced contains one-third of its volume of oxygen; in the case of nitric oxide, one-half.

151. Nitrogen peroxide, NO_2 (N_2O_4).—Some lead nitrate is placed in a retort and heated gently. The gases given off are passed into a U-shaped tube surrounded by a mixture of ice and salt (Fig. 32). The lead nitrate is decomposed according to the following equation:

$$Pb(NO_3)_2 = PbO + 2NO_2 + O.$$
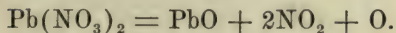
The nitrogen peroxide condenses in the U-tube, the oxygen passing on unchanged.

Nitrogen peroxide is, at low temperatures, a white solid which melts to a colorless liquid. If the temperature is allowed to

Fig. 32.—Preparation of nitrogen peroxide, NO_2.

rise the liquid becomes yellow, and is finally converted into a gas which at —10° is faint yellow, nearly colorless. If the gas be heated the tint deepens, until at 140° it possesses a reddish-black color so intense that a layer 2 centimetres thick is opaque.

This variation in properties with the temperature is surprising, but its cause becomes clear when the density of the gas is deter-

mined at different temperatures. When this is done it is found that the molecular weight of the colorless gas corresponds to the formula N_2O_4, while the deep reddish-black gas obtained at 140° has a molecular weight only half as great and possesses the formula NO_2. Nitrogen peroxide, then, exists in two conditions: as N_2O_4, which is colorless, has the molecular weight 92, and the density 46 referred to hydrogen; and as NO_2, which is reddish black, has the molecular weight 46, and the hydrogen density 23. When the substance is heated, the reaction—

$$N_2O_4 = 2NO_2—$$
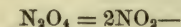
occurs, and the color becomes deeper as the temperature rises, because the quantity of NO_2 in the gas increases. Finally, at 140°, the change is complete, and then heating to a higher temperature does not make the color more intense. On cooling, the change is reversed. This is an interesting case of *dissociation*, or "gradual decomposition, increasing with the temperature and reversed by cooling." It is important to understand clearly the distinction between N_2O_4 and NO_2.[1] Both have exactly the same composition. If we think of matter in mass, then the difference is that N_2O_4 has a density twice as great as that of NO_2. If we think of molecules, then the molecule N_2O_4 is twice as heavy. We express this by saying that N_2O_4 is a *polymer* of NO_2. It will be seen that we have already studied a very similar state of things in the relation between ozone and oxygen.

152. *Nitrogen pentoxide*, N_2O_5, can be obtained by abstracting the elements of water from nitric acid, HNO_3:

$$2HNO_3 - H_2O = N_2O_5.$$
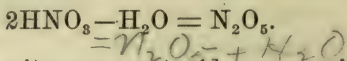
In preparing nitrogen pentoxide, pure nitric acid is mixed with phosphorus pentoxide, P_2O_5, and the mixture distilled. Nitrogen pentoxide is a colorless crystalline substance which is very unstable, and explodes spontaneously on being preserved. When thrown into water the liquid becomes hot, and is found to contain nitric acid:

$$N_2O_5 + H_2O = 2HNO_3.$$

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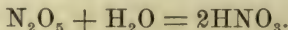
[1] This will be better understood after reading Chapter XVI.

153. Nitric acid, HNO_3, is obtained by distilling a mixture of sodium nitrate, $NaNO_3$, with sulphuric acid. In the laboratory the reaction can be carried out in the apparatus shown in Fig. 33. The vapor of the acid liberated in the retort is led into a glass vessel around which cold water circulates. Here it condenses to a liquid.
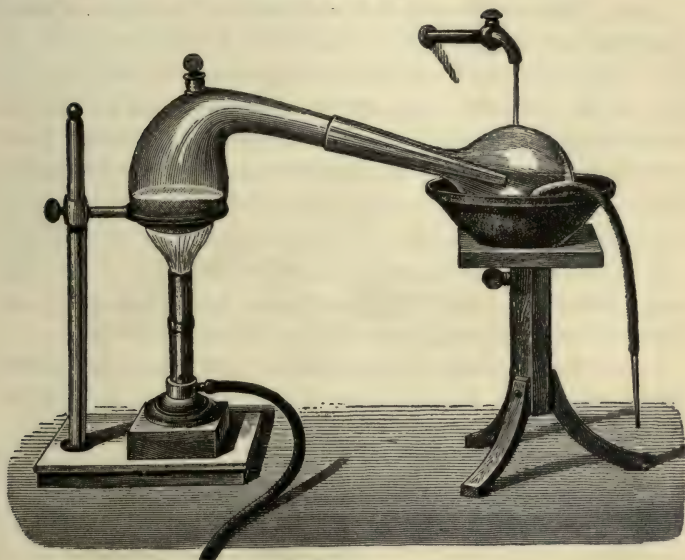

FIG. 33.—Preparation of nitric acid.

On the large scale, cylinders of cast iron are employed to contain the mixture of sodium nitrate and sulphuric acid, and the condensation of the nitric acid is effected in stoneware bottles. The equation is:

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

154. Properties.—Pure nitric acid is a colorless, fuming liquid, about one and one-half time as heavy as water. Its vapor has an acrid odor and is poisonous, and the liquid attacks the skin and produces all the effects of a violent irritant poison when swallowed. It attacks many metals,

9

converting some, like copper and silver, into their nitrates (e. g., silver nitrate, $AgNO_3$), others, like tin, into their oxides (e. g., SnO_2). Still others, like gold and platinum, are not affected by it. *Hydrogen is never liberated by the action of nitric acid upon a metal.* Usually the gas given off is NO or NO_2. With cold dilute acid, N_2O is obtained.

155. **Uses.**—Nitric acid is a commercial product of some importance. Considerable quantities of it are employed in the manufacture of nitroglycerin and guncotton, and the use of the acid for this purpose has increased of late on account of the production of smokeless gunpowders, most of which are mixtures containing guncotton or guncotton and nitroglycerin. It is also employed in etching metallic surfaces, and to some extent in the separation of gold and silver. From an alloy of these two metals it dissolves the silver to nitrate ($AgNO_3$), leaving the gold unaffected. At present, sulphuric acid is replacing it in this operation.

156. **The nitrates.**—The salts of nitric acid are called the nitrates, and, like the salts of all acids, each consists of the acid with its hydrogen replaced by some metal, e. g.,

Nitric acid
HNO_3.

KNO_3, potassium nitrate;
$NaNO_3$, sodium nitrate;
$Cu(NO_3)_2$, copper nitrate;
$Bi(NO_3)_3$, bismuth nitrate.

The nitrates are all soluble in water and are all decomposed by heat, leaving a residue, which usually consists of the oxide of the metal whose nitrate was heated. If this oxide is itself decomposed by heat, the metal is obtained instead. Thus, silver nitrate first melts, then gives off NO_2 and oxygen, and leaves a residue of silver.

157. **Potassium nitrate,**, KNO_3, commonly called saltpeter, occurs as an incrustation on the soil in hot countries. It consists of white crystals, very soluble in water, which melt easily when heated to a colorless liquid. This salt

was formerly made in large quantities for the manufacture of black gunpowder. This is a mixture of about the following composition:

Potassium nitrate............ 75 per cent;
Charcoal .... 15 "
Sulphur .... 10 "

Black gunpowder is still largely employed for saluting purposes and for hunting. In warfare it is obsolete.

158. **Sodium nitrate**, $NaNO_3$, is by far the most important salt of nitric acid commercially. In the rainless region in the northern part of Chile, near the junction with Peru and Bolivia, immense deposits of this salt occur, and about 1,500,000 tons of it are exported yearly. About three-fourths of this are employed as a fertilizer, in order to furnish nitrogen to crops; the remainder goes into the chemical industries, being used chiefly in the manufacture of nitric acid and of potassium nitrate.

Sodium nitrate is white, and is more soluble in water than potassium nitrate. It deliquesces in moist air, which is not the case with the potassium salt.

159. *Nitrous acid*, HNO_2.—When sodium nitrate is carefully heated, one-third of its oxygen escapes and the residue has the composition $NaNO_2$. It is called sodium nitrite. Potassium nitrate behaves in the same way, leaving a residue of potassium nitrite, KNO_2. Many other nitrites are known, most of which, like potassium and sodium nitrites, are colorless or faint yellow, and freely soluble in water. Silver nitrite is only slightly soluble, and separates as a white precipitate when solutions of potassium nitrite and silver nitrate are mixed:

$$KNO_2 + AgNO_3 = AgNO_2 + KNO_3.$$
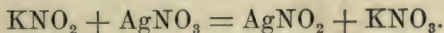
These compounds are regarded as salts of *nitrous acid*, HNO_2, but the acid itself has never been prepared. It is

only known dissolved in water, and when we attempt to obtain it by evaporating the liquid it decomposes:

$$2HNO_2 = H_2O + NO + NO_2.$$
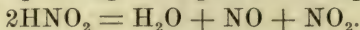
160. Compounds of nitrogen with chlorine, bromine, and iodine.—When chlorine is passed into a solution of ammonium chloride, nitrogen chloride, NCl_3, is produced:

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$
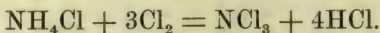
Nitrogen chloride is a yellow oil with a penetrating odor. Its vapor attacks the mucous membranes, and by prolonged inhalation produces permanent inflammation. The liquid explodes violently on being heated and also on contact with many substances; for instance, with rubber or oil of turpentine. Sometimes it seems to explode spontaneously. The explosion is simply a sudden separation into nitrogen and chlorine, a process which is accompanied by great expansion and liberation of heat.

Nitrogen bromide, NBr_3, is very imperfectly investigated. It is said to be a red oil which explodes like the chloride.

The analogous compound with iodine would be NI_3. This is unknown, but a compound, $N_2H_3I_3$, has been studied, and this we can regard as consisting of a molecule of NI_3 combined with a molecule of ammonia; thus, NH_3,NI_3. It forms dark crystals with a coppery, metallic luster. It is extremely explosive.

CHAPTER XVI

ATOMIC AND MOLECULAR WEIGHTS—AVOGADRO'S RULE

161. **The molecular weight of HCl.**—When we analyze hydrochloric acid we find that it contains for 1 part of hydrogen 35.5 parts of chlorine. If, then, we assume that it contains one atomic weight of each element, it follows at once that the atomic weight of chlorine is 35.5. It would lead us too far to discuss here the reasons for accepting this as the real atomic weight of this element. We will content ourselves with the statement that, by assigning the value 35.5 to the atomic weight of chlorine, we can write simple formulas for all the chlorine compounds. *We are never compelled to use fractional parts of a symbol in writing these formulas.*

HCl is, then, the formula of hydrochloric acid, and when we add together the parts by weight indicated in the formula, we obtain:

$$H = 1.$$
$$Cl = 35.5$$
$$\overline{}$$
$$HCl = 36.5$$

This figure, 36.5, we call the *molecular weight* of the substance. From the standpoint of the atomic theory, HCl means an atom of hydrogen in union with an atom of chlorine, forming a *molecule* of hydrochloric acid, and this molecule must weigh 36.5 times as much as the hydrogen atom. We do not know what the atom of hydrogen weighs, but if we assume it to weigh one ten-millionth of a milligram, then

the molecule HCl would weigh 36.5 ten-millionths of a milligram.

Returning to grams, the formula HCl means 36.5 grams of a substance which consists of 1 gram of hydrogen and 35.5 grams of chlorine. The volume which these 36.5 grams of hydrochloric-acid gas will occupy depends upon the temperature and the pressure; at the standard temperature, 0°, and the standard pressure, 760 millimeters of mercury, the volume is 22.4 liters.

Now, *the volume occupied by the molecular weights in grams of all gases and vapors is the same, at the same temperature and pressure; and this volume is 22.4 liters if the temperature is 0° and the pressure 760 millimeters.* For example:

Name of gas.	Formula.	Molecular weight.	Volume of mol. weight.
Hydrochloric acid................	HCl	36.5	22.4 liters.
Ammonia........................	NH₃	17	22.4 "
Nitrous oxide...................	N₂O	44	22.4 "
Nitric oxide....................	NO	30	22.4 "

162. Calculations based on the rule stated above.—This fact, that the volume of the molecular weight, taken in grams, is the same for all gases and vapors—22.4 liters at 0° and 760 millimeters—gives us a simple method of calculating the weight of one liter of any gas. We have only to divide the molecular weight by 22.4. Thus, the weight of 1 liter of nitrous oxide, N_2O, is $\frac{44}{22.4} = 1.9642$ gram. The same fact enables us to determine at once from the formula the density of any gas or vapor referred to hydrogen as unity. The formula of hydrogen is H_2. The molecular weight is therefore 2, and it requires 2 grams of the gas to fill the same volume as the molecular weights of other gases. But the density of any gas referred to hydrogen is simply the weight of any volume of it divided by the weight of the same volume of hydrogen. The density is therefore

equal to the molecular weight divided by the 2 grams of hydrogen which fill the same bulk. If D = density and M = molecular weight, we have therefore—

$$D = \frac{M}{2}.$$

Thus, the molecular weight of nitrous oxide is 44 and the density is $\frac{44}{2} = 22$. Any volume of the gas weighs 22 times as much as the same volume of hydrogen, both being at the same temperature and pressure.

163. **The molecular weight can be calculated by multiplying the density by 2.**—Of course, if we determine the density of a gas or vapor by experiment, we can calculate the molecular weight by multiplying the density by 2, and this is a most important method of ascertaining the molecular weights of new substances whose formulas have not yet been established. By weighing a measured volume of pure nitrous oxide we could easily show that its density, referred to hydrogen, is about 22, and from this it follows that the molecular weight is 22 × 2, or 44.

164. **Avogadro's rule.**—We have just stated that the molecular weights of all gases and vapors occupy the same volume, temperature and pressure being the same. Let us now translate this statement into the language of atoms and molecules. In the first place, it is clear that the molecular weights, taken in grams, of all substances, must contain the same number of molecules.

In order to understand this statement, think of any substance which consists of individual grains all of which are alike—of shot, for instance. Let us consider that we have several different kinds of shot, and that we are required to choose quantities by weight of the different kinds which will contain the same number of pellets. We will take one decigram (.1 gram) as our unit of weight, and suppose that each grain of the first kind of shot weighs 2 decigrams (.2 gram). Then 2 kilos will contain $\frac{2000}{.2}$, or 10,000 pellets. Each

grain of a second sort weighs 10 decigrams or 1 gram. How much of this variety will be required to contain 10,000 pellets ? Clearly 10 kilos, for each kilo will contain 1,000. Finally, if we imagine a third variety, consisting of bullets each of which weighs 100 decigrams, or 10 grams, it is plain that in order to obtain 10,000 bullets we must weigh off 100 kilos, for each kilo will contain $\frac{1000}{10}$, or 100.

What is true of the visible shot is equally true of the invisible molecules.

$$
\begin{array}{llll}
17 & \text{grams of} & & \text{ammonia, } NH_3, \\
44 & \text{``} & \text{``} & \text{nitrous oxide, } N_2O, \\
30 & \text{``} & \text{``} & \text{nitric oxide, } NO, \\
2 & \text{``} & \text{``} & \text{hydrogen, } H_2,
\end{array}
$$

must all contain the same number of molecules. But we have seen that these quantities occupy equal volumes. Hence, in these equal volumes equal numbers of molecules are contained. In general, the argument is this:

1. The molecular weights in grams of all substances contain equal numbers of molecules.

2. The molecular weights in grams of all gases and va- pors occupy equal volumes at the same temperature and pressure. Therefore—

3. *In equal volumes of all gases and vapors at the same temperature and pressure, equal numbers of molecules are contained.* This statement is commonly called *Avogadro's rule.*

The density of a gas is the weight of any volume of it divided by the weight of the same volume of hydrogen. It is therefore the weight of a certain number of molecules of the gas divided by the weight of the same number of molecules of hydrogen. But this is the same thing as the weight of one molecule of the gas divided by the weight of one molecule of hydrogen. Thus the density of nitrous oxide is—

$$\frac{\text{Weight of one molecule, } N_2O}{\text{Weight of one molecule, } H_2} = \frac{44}{2} = 22.$$

But, since all our atomic weights are in terms of the weight of the hydrogen atom as 1, the molecular weight of nitrous oxide is—

$$\frac{\text{Weight of one molecule, } N_2O}{\text{Weight of one atom, } H} = \frac{44}{1} = 44.$$

Again, we see that the density is half the molecular weight. In determining the molecular weights our unit is the hydrogen atom, $H = 1$; in determining the densities, it is the hydrogen molecule, $H_2 = 2$.

165. **The law of simple volume ratios.**—We have noticed (p. 80) that, when two gases combine, there is always a simple relation between the volumes of the gases entering into the change. This is just what the atomic theory would lead us to expect. Chemical combinations take place between molecules, and the number of molecules of each substance entering into the change is always small. Equal volumes of gases contain equal numbers of molecules. If one molecule of one gas combines with one molecule of the second, then one volume of the first will combine with one volume of the second, thus—

$$H_2 + Cl_2 = 2HCl.$$
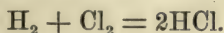
On the other hand, in the production of water, two molecules of hydrogen react with one of oxygen; therefore, two volumes of hydrogen react with one of oxygen:

$$2H_2 + O_2 = 2H_2O.$$
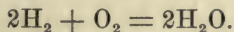
In other words, so far as gases and vapors are concerned, the formulas in the equation, which represent molecules, can be also read as representing *volumes*.

166. **Doubled formulas.**—Finally, we must inquire why it is that in some cases we express the composition of substances by formulas which are multiples of the simplest expressions which would serve that purpose. Thus, for hydrogen peroxide we write H_2O_2, for hydrazine N_2H_4,

when the formulas OH and NH_2 would mean exactly the same thing, so far as chemical composition goes.

A doubled formula means usually that the density of the gas or vapor has been determined, and from this, by multiplying by 2, the molecular weight; and that the latter has been found to be twice that which the simplest formula requires. Thus, there is a gas called cyanogen which contains 12 parts of carbon in union with 14 of nitrogen. Its composition is therefore accurately expressed by the formula CN. But its density referred to hydrogen is 26, and therefore the molecular weight must be 26×2, or 52. Accordingly, we must write for the gas the doubled formula C_2N_2.

With hydrogen peroxide we can not ascertain the molecular weight in this way, because when we attempt to convert it into vapor to obtain the density, it separates into oxygen and water. Many other substances behave in the same way. But within the last few years methods have been devised by which it is possible to determine the molecular weights of *dissolved substances*. Thus, when hydrogen peroxide is dissolved in water, its molecular weight is found to be 34, and this requires us to write the formula H_2O_2, not HO.

When a substance can neither be dissolved nor vaporized without decomposition, both these methods of determining the molecular weight fail. Such a substance is mercuric oxide. At present the question whether it should be written HgO or Hg_2O_2, or some higher multiple, is one to which we can not return an answer. Therefore we use the simplest formula for the present. The problem of determining the molecular weights of such substances is now being attacked, and the result so far is that no multiplying is necessary; the molecular weight obtained corresponds to the simplest formula which will express the composition accurately. There is no reason, therefore, to consider the molecules of solids as large and heavy compared with those of gases.

CHAPTER XVII

ACIDS, BASES, AND SALTS—ELECTROLYTIC DISSOCIATION— METALS AND NON-METALS

167. Some strong solution of sodium hydroxide is placed in a beaker and strong hydrochloric acid is carefully added to it. There is an energetic reaction, the liquid becomes very hot, and a white powder of common salt separates:

$$NaOH + HCl = NaCl + H_2O.$$
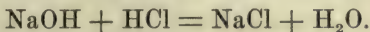
A few drops of the same sodium hydroxide solution are placed in a test-tube, and sulphuric acid added, one drop at a time. Each drop of the acid hisses when it strikes the liquid like water falling upon red-hot iron. Great heat is evolved, and white crystals of sodium sulphate are produced:

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$
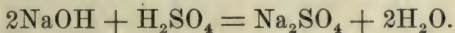
Sodium hydroxide is a *base,* and HCl and H_2SO_4 are acids, and these two experiments will serve as illustrations of what happens when an acid and a base come into contact. A chemical change occurs. Water is one product and the other is a substance called a salt, which consists of the acid, with its hydrogen replaced by the metal of the base.

168. **Bases.**—The bases are hydroxides of the metals or of some group of atoms—NH_4, for instance—which plays the *rôle* of a metal. When a base is dissolved in water the solution has a bitter, burning taste and a caustic effect upon the skin and other tissues, which is stronger the stronger the base and the more concentrated the solution. There are various sensitive coloring matters called *indicators,* whose

colors change remarkably when a base acts upon them. Thus, a water solution of red *litmus* is turned deep blue by a little sodium hydroxide or other base; a solution of cochineal, orange itself, turns violet.

169. Acids.—*Acids* are compounds containing hydrogen which can be replaced by metals, producing salts. Acids have a sour taste—the acid taste—similar to that of vinegar or lemon juice, and strong acids have an energetic caustic action upon organic tissues. Acids reverse the color changes which bases produce with indicators. Litmus, which has been turned from red to blue by a base, is again colored red by an acid; cochineal, which has been colored violet by a base, again becomes orange when an acid is added.

170. Neutralization.—The reaction between an acid and a base in which a salt and water are produced is called *neutralization*. From the equation—

$$NaOH + HCl = NaCl + H_2O,$$
$$40 \qquad 36.5 \qquad 58.5 \qquad 18,$$
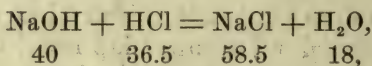
in which the numbers written below are the molecular weights of the substances, it is clear that *if hydrochloric acid and caustic soda are mixed in exactly the right quantities, the liquid will contain neither substance; it will contain only salt and water.* Thus, if we dissolve 40 grams of pure sodium hydroxide in water, coloring the liquid with a little litmus, and then add gradually 36.5 grams of hydrochloric acid dissolved in water, the litmus will remain blue until all the hydrochloric acid is added. At this point the liquid contains nothing but sodium chloride and water. One drop of acid in excess of this quantity will instantly change the color to red.

171. Salts.—A *salt* is the product of the chemical change between an acid and a base. It is a compound derived from an acid by replacing the hydrogen by a metal, e. g.:
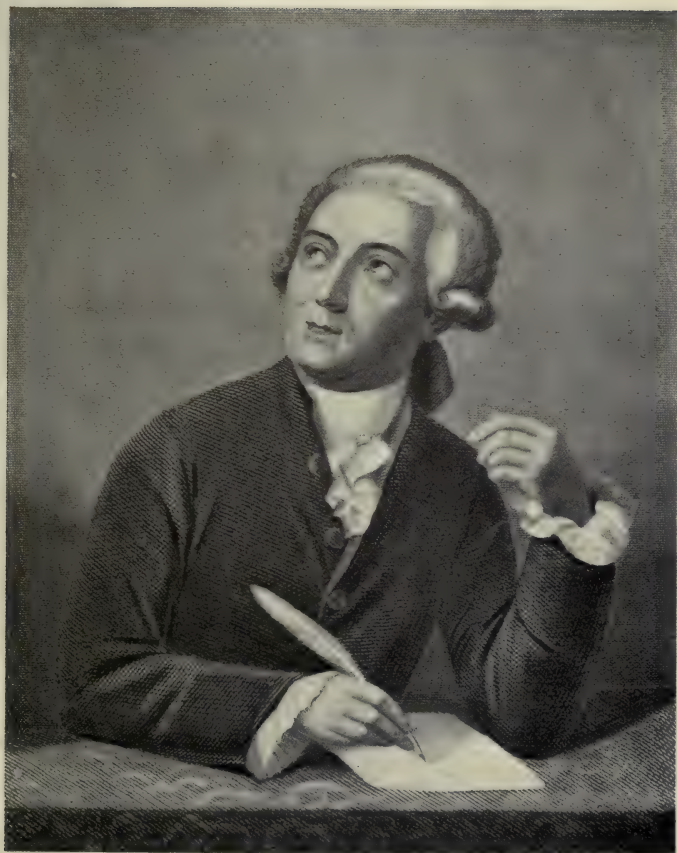
ANTOINE LAURENT LAVOISIER
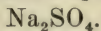B. Paris, 1743.   D. on the scaffold, 1794.

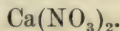| Sulphuric acid	Sodium sulphate	Calcium sulphate
H_2SO_4.	Na_2SO_4.	$CaSO_4$.
Nitric acid	Sodium nitrate	Calcium nitrate
HNO_3.	$NaNO_3$.	$Ca(NO_3)_2$.

Salts have a saline taste which is quite different from the sour taste of the acids and the bitter taste of the bases. *A solution containing only a salt and water has no effect upon the color of indicators.* Some salt solutions appear to contradict this statement. Thus, if we dissolve pure copper chloride in water the liquid reddens litmus. In this case the solution contains hydrochloric acid, which has been produced by the reaction of a small portion of the copper chloride with water:

$$CuCl_2 + 2H_2O = Cu(OH)_2 + 2HCl.$$
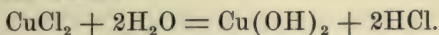
On the other hand, when potassium cyanide, KCN, is dissolved in water, the solution turns red litmus blue. This is because some of the potassium cyanide has reacted with the water:

$$KCN + H_2O = KOH + HCN,$$
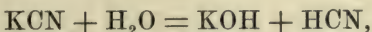
and the liquid contains potassium hydroxide, an extremely strong base. This partial decomposition of salts by water is called *hydrolysis*. It is frequent with salts of weak acids and bases.

172. Acids only show their peculiar properties in presence of water.—It is reasonable to ascribe the peculiar qualities of acids to the hydrogen which they all contain. But the remarkable properties of acids are only manifested in water solution (compare p. 82). Acids free from water do not affect indicators, and are inert toward many substances upon which we should expect them to act. Thus, when they are brought into contact with metals, either there is no reaction or the reaction is quite different from that which takes place when the same metal is treated with a water solution of the same acid. Further, there are thousands of substances containing hydrogen which are not

acids. Alcohol, C_2H_6O, for example, when dissolved in water, yields a solution which has no acid taste, does not affect the color of indicators, and does not exhibit any of the chemical behavior of an acid.

Acids, then, differ from other substances in this respect, that they contain hydrogen, which, in water solution, is in a different state from the hydrogen of other compounds. What is the difference?

173. **Solutions of acids in water conduct the electric current.**—A solution of alcohol in water is an insulator; it does not allow the electric current to pass. Liquid, water-free hydrochloric acid behaves in the same way. On the other hand, the current is freely transmitted by a water solution of hydrochloric acid, and its transmission is carried on by a stream of hydrogen particles which pass to the negative pole, give up their electric charges to the electrode, and are liberated as gas, and a procession of chlorine particles, which move to the positive pole and are there relieved of their charges and liberated in the same way. It appears, then, that the hydrogen and chlorine atoms in a water solution of hydrochloric acid exhibit an independence of each other, a readiness to move in different directions, which we do not find in the anhydrous substance. In connection with this we must think of the inertness of the anhydrous substance and the great chemical activity of the water solution. This activity is associated with the ability to conduct the current, for HCl dissolved in chloroform is a non-conductor, and is just as inactive chemically as the anhydrous substance.

174. **Ions.**—Facts of this kind have led chemists to picture to themselves the state of things in a water solution of hydrochloric acid somewhat in this way. A large proportion of the acid exists no longer as molecules HCl, but as atoms H and Cl. Each H atom has a positive charge and each Cl atom a negative charge, and they move about quite

independently of each other. When the electrodes from the battery are dipped into the liquid the H atoms with their positive charges naturally move to the negative pole, for the same reason that a positively charged pith-ball is attracted by a negatively charged stick of sealing-wax. Here they yield up their charges and the discharged atoms unite in pairs to molecules of ordinary hydrogen H_2, which is liberated. The same thing happens with the chlorine at the positive pole. These charged atoms we shall call *ions,* and it is impossible to obtain a liquid containing hydrogen ions or chlorine ions alone, because no positive charge can exist anywhere without an equivalent negative charge in the neighborhood, and *vice versa.* Although the hydrogen and chlorine in a water solution of hydrochloric acid exist largely as separate ions $\overset{+}{H}$ and $\overset{-}{Cl}$, yet we must not expect the solution to exhibit the odor and bleaching action of chlorine, nor the combustibility and other properties of hydrogen. For the properties of ordinary chlorine are those of a substance composed of molecules Cl_2, and the water solution of hydrochloric acid does not contain these molecules. It contains the ions $\overset{-}{Cl}$ with their negative charges—quite a different thing. The same statement applies to the hydrogen.

175. **Difference between strong and weak acids.**—The properties of acids, as a class, are those of the hydrogen ions, and the strongest acids are those in which hydrogen ions are most abundant—that is, those in which the separation sketched above is most complete. In a solution of a very strong acid, like HCl, a large fraction of the substance is separated—almost all of it in a somewhat dilute solution —and the liquid strongly exhibits those peculiar properties which are due to the presence of hydrogen ions—acid properties, we call them. On the other hand, in a solution of a weak acid (like HCN, prussic acid), the amount of separation is slight. Most of the acid still exists as molecules

HCN, the number of hydrogen ions is small, and the acid properties feeble. Since the passage of the electric current through the liquid is carried on by means of the ions, it follows that a solution of a strong acid—one very much separated into ions—will conduct well, while a solution of a weak acid—one in which the separation is slight—will conduct badly. *Hence, the strength of an acid can be measured by its ability to conduct the current. The more marked the acid properties the more readily the electric current will pass through the water solution of the substance.*

176. Solutions of bases contain hydroxyl ions, $\overset{-}{OH}$.—The same views apply to bases. Since the bases are all hydroxides, their peculiar properties are those of hydroxyl, OH, and in solutions of the bases the hydroxyl exists as an ion, $\overset{-}{OH}$.[1] In water solutions of a strong base, like NaOH, the separation into ions ($\overset{+}{Na}$ and $\overset{-}{OH}$) is almost complete, the hydroxyl ions are numerous, and the basic properties strongly in evidence. In solutions of weak bases (NH_4OH will serve as an instance), the separation into ions ($\overset{+}{NH_4}$ and $\overset{-}{OH}$) is slight, the hydroxyl ions few, and the basic properties feeble. Finally, there are many hydroxides (alcohol, which we may write C_2H_5OH this time, is again a good example) where there is no separation into ions when the substance is dissolved, and therefore no basic properties. In striking agreement with this is the fact that *solutions of strong bases are good conductors of the electric current, solutions of weak bases bad conductors, and solutions of hydroxides, like alcohol, which are not bases at all, non-conductors.*

177. Ions of salts.—Salts are also separated into ions when dissolved in water, and therefore their solutions con-

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[1] We shall indicate the charges of the ions by small + and − signs placed above.

duct the current. Nickel chloride, $NiCl_2$, for instance, exists in solution separated into two chlorine ions, $\overset{-}{Cl}\ \overset{-}{Cl}$, and one nickel ion, which must have twice as much positive electricity on it as one chlorine ion has of negative. We can write it $\overset{++}{Ni}$. All solutions of nickel salts have the same green color, and our theory of ions easily explains this fact, for this color is simply that of the nickel ion. Otherwise it would be astonishing that salts so different in composition as nickel chloride ($NiCl_2$), nickel sulphate ($NiSO_4$), and nickel nitrate ($Ni(NO_3)_2$) should produce exactly the same color. When the current is passed through a solution of nickel chloride, the chlorine ions proceed to the positive pole, where they yield up their charges and are liberated as chlorine gas, just as in the case of hydrochloric acid. The nickel ion carries its positive charge to the negative pole, where it gives it up and is converted into ordinary metallic nickel, which adheres to the electrode. Table salt in solution is separated into ions $\overset{+}{Na}$ and $\overset{-}{Cl}$, and when the current passes through it, the chlorine is liberated at the positive pole. But it is impossible for sodium to be liberated at the other pole on account of the presence of water. Hence, at the negative pole, hydrogen from the water escapes instead.

178. *Acids, bases, and salts are the only substances whose solutions conduct the current, and the only substances, therefore, which separate into ions when dissolved.* An ion may be an atom or a group of atoms. Thus, the ions of hydrochloric acid are simply $\overset{+}{H}$ and $\overset{-}{Cl}$, but those of nitric acid are $\overset{+}{H}$ and $\overset{-}{NO_3}$, and those of sulphuric acid (H_2SO_4) are $\overset{+}{H}$, $\overset{+}{H}$, and $\overset{--}{SO_4}$.

This idea of the separation of dissolved substances into ions has thrown a flood of light upon chemical and physical changes in which acids, bases, or salts are concerned. It is

10

called the *theory of electrolytic dissociation.* The student who pursues chemical studies further will meet with it again.

179. Metals and non-metals.—When we compare elements like copper and silver, on the one hand, with elements like sulphur and phosphorus, on the other, certain differences force themselves on our attention. The most noticeable distinction is the appearance. A polished surface of copper or silver reflects almost all the light which falls upon it, and this gives to it what is called the *metallic luster.* Again, a piece of silver when struck heavily with a hammer flattens out, and with care can be beaten into a thin sheet; a piece of sulphur flies to pieces. The silver is *malleable,* the sulphur *brittle.*

Elements like copper and silver are called *metals*; elements like sulphur and phosphorus *non-metals.*

180. Physical properties of metals.—The metals have a peculiar luster—the metallic luster. They are far better conductors of heat and of the electric current than the non-metals. The metals can be drawn into wire and beaten out with the hammer—that is, they are ductile and malleable. Gold can be beaten into leaf so thin that a pile containing a hundred thousand sheets in contact would be less than one centimeter in height, and one gram of gold can be drawn into a wire three thousand meters in length. All of the other metals are inferior to gold in these properties, and in some—lead and bismuth, for instance—malleability and ductility are slight. These two properties, together with the tenacity (toughness) of the metals, are the chief source of their great importance in commerce. The non-metals are immensely behind the metals in all three respects.

181. Chemical distinctions.—The hydrogen compounds of the non-metals are *gases*—water, which is a liquid easily converted into a vapor, is the chief exception—and they are

rather stable substances which show no very marked tendency to separate into their constituents. Ammonia and hydrochloric acid are good examples. On the other hand, many of the metals do not form hydrogen compounds at all, and when they do, the substances are solids and decompose readily into hydrogen and the metal.

The hydroxide of a metal is a base, and when it dissolves in water it separates into positively charged metal ions and negatively charged hydroxyl ions. Thus, a water solution of potassium hydroxide (KOH) contains potassium ions positively charged ($\overset{+}{K}$) and hydroxyl ions charged negatively ($\overset{-}{OH}$). A solution of calcium hydroxide, $Ca(OH)_2$, consists of calcium ions with a double positive charge ($\overset{++}{Ca}$) and twice as many hydroxyl ions, each with its negative charge $\left(\begin{matrix}\overset{-}{OH}\\ \overset{-}{OH}\end{matrix}\right)$.

Since the solutions of the metallic hydroxides contain hydroxyl ions, they turn red litmus blue and exhibit the other properties which we have learned to associate with bases (p. 125). Many of the metallic hydroxides are insoluble in water—nickel and copper hydroxides, for example—and these can not act upon the indicators; but they can still be considered as bases in the sense that they react readily with acids, forming salts.

182. **Metals tend to form positively charged ions.**—This tendency of the metals to exist in solution as positively charged ions is by no means restricted to the hydroxides. We have seen that in a solution of table salt there are sodium ions ($\overset{+}{Na}$) and chlorine ions ($\overset{-}{Cl}$), and in the water solution of every salt the metal is present in this condition. A metal never exists alone as a *negatively* charged ion in solution, and therefore never proceeds alone to the positive pole when the current is passed through the liquid—always

to the negative pole. We may say, therefore, that a metal is a substance which has a tendency to exist alone in solution as a positively charged ion. It must not be inferred from the word " alone " in the above statement that there can be such a thing as a solution containing positively charged metal ions without any corresponding negative ions. This is impossible, for in every solution the number of positive and negative charges must be exactly the same. We mean simply that the metal atom moves about independently in the liquid with its positive charge, and proceeds alone to the negative pole in electrolysis. This behavior we can sum up by saying that the *metals are electropositive.*

183. **The hydroxides of the non-metals are acids.**—Many of the hydroxides of the *non-metals* are unstable or unknown, but those which exist are *acids*; and, since the properties of an acid liquid are simply those of the hydrogen ions, they must separate when dissolved in quite a different way from the metallic hydroxides. Chlorine hydroxide (ClOH), which is called *hypochlorous acid,* is an example. Its separation when dissolved is into hydrogen ions ($\overset{+}{H}$) and ions ($\overset{-}{ClO}$). An atom of a non-metal can never exist alone as a positively charged ion, only as a negatively charged one, and therefore can never proceed by itself to the negative pole when the current is passed—only to the positive. We can sum up this behavior in the statement that the *non-metals* are *electronegative.* It follows from this that there can be no such thing as a salt in which a single non-metallic atom is the positive constituent, no such thing as a nitrate of chlorine, $ClNO_3$, or a sulphate of bromine, Br_2SO_4. Such a compound is a chemical impossibility. *Only the metals form salts with acids.*

CHAPTER XVIII

THE SODIUM GROUP

This group contains the following five elements:

Lithium, Li. Rubidium, Rb.
Sodium, Na. Cæsium, Cs.
Potassium, K.

184. General properties.—This group contains, from the chemical standpoint, the most positive metals known. Much of what we have learned about sodium is true of all five. They are soft enough to be cut with a knife, are excellent conductors of heat and electricity, and possess small densities. Lithium, the lightest, is little more than half as dense as water, and, except solid hydrogen, is the lightest of all solids. These elements possess a strong silver-white metallic luster which is permanent when the specimen is sealed up in dry hydrogen, but rapidly disappears in the air. This is due to the oxygen of the air, which acts upon the surface, producing the oxide of the metal, and still more to the water-vapor, which produces the hydroxide.

185. Reaction with water.—When one of these metals comes in contact with water, hydrogen is given off and the hydroxide of the metal dissolves in the excess of water. We have studied this action in the case of sodium:

$$Na + H_2O = NaOH + H.$$
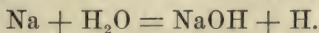
The same change occurs with the others. If we indicate an atom of any one of the five by M, we can write an equation—

$$M + H_2O = MOH + H,$$

135
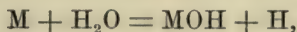
which describes their conduct with water, and the equation for a particular metal is obtained by substituting the symbol of that metal for M on both sides of the expression.

The energy of the reaction with water increases with increasing atomic weight. Lithium evolves hydrogen rapidly, but does not melt. Sodium melts to a globule which runs about on the surface of the water, but the temperature does not rise high enough to inflame the hydrogen. In the case of potassium the hydrogen catches fire. Rubidium and cæsium react with water with explosive violence.

186. Occurrence.—Of course elements like those of this group—energetically acted upon by oxygen and water—are not found free in nature. Compounds of sodium and potassium are abundant, the other three are rare. Lithium, though it nowhere occurs in large quantities, is quite widely distributed. Traces of it are contained in many soils, in sea-water and most natural waters, in plants (for instance, in tobacco, coffee, sugar-cane, and seaweed), and even in substances of animal origin (in blood and milk, for example). This wide distribution is the rule with elements of small atomic weight ($Li = 7$).

187. Tendency to form positive ions.—In the violence with which the metals of this group react with water—forming their hydroxides—we see the strong tendency of their atoms to assume the state of positively charged ions in solution, and this tendency is greater in this group than anywhere else. This is another and better way of saying that in these elements the metallic properties are most highly developed. We shall not be surprised, therefore, by the fact that the hydroxides of these metals are the strongest bases known to chemical science, for this tendency of the metal atom will cause the hydroxide to cleave very completely into positively charged metal ions and negatively charged hydroxyl ions when dissolved in water. Hydroxyl ions will therefore be numerous in the liquid, and the char-

acteristic properties which they communicate to a solution will be strongly marked—in other words, *the dissolved substance will be a strong base.* In this case, as in most other groups composed of metals, the strength of the base increases with the atomic weight of the metal. Cæsium hydroxide, CsOH, is the strongest of all bases.

188. Salts containing the metals of this group are almost all freely soluble in water. The ions of all five elements are colorless, and accordingly solutions containing salts of these metals are colorless also, unless the acid ion possesses a color.

189. **Lithium, Li = 7.**—Lithium is a silver-white metal, harder than sodium. It oxidizes readily in the air, but not so rapidly as the other members of the subgroup. Thrown into water, it is rapidly converted into its hydroxide—

$$Li + H_2O = LiOH + H—$$
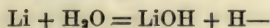
but the temperature does not rise high enough to melt the metal. Heated in the air or in oxygen, it burns with intense white light to lithium oxide, Li_2O.

Lithium chloride, LiCl, is white, deliquescent, and very soluble in water. Some mineral waters contain considerable quantities of it, and such waters are employed with advantage in rheumatic troubles.

190. **Valence.**—An atom of lithium is equal in combining power to an atom of hydrogen. Thus it replaces hydrogen atom for atom in water:

Water	Lithium hydroxide
HOH,	LiOH,

in hydrochloric acid:

Hydrochloric acid	Lithium chloride
HCl,	LiCl,

and in all other acids. The combining power of an element has received the name of *valence,* and if we call the combining power of hydrogen *one,* we can describe this state of things by the statement that lithium also has a valence

of one, or is *univalent*. The great advantage of putting the matter in this way is that it enables us to write at once the formula of any lithium salt if we know that of the corresponding acid. All that is necessary is to replace each hydrogen atom by an atom of lithium. Thus:

Sulphuric acid	Lithium sulphate
H_2SO_4.	Li_2SO_4.
Nitric acid	Lithium nitrate
HNO_3.	$LiNO_3$.

The five metals of this group are univalent in almost all their compounds; and if we remember this, it is unnecessary to memorize the formulas of their salts, for we can write them in the same way as we have done with lithium sulphate and nitrate. Thus, the idea of valence is a valuable labor-saving device in dealing with elements like these, whose valence remains the same. The atoms of some elements, like nitrogen, vary in combining power in different compounds, and then the advantage of the notion of valence is not so great. We are compelled to learn the formula of each compound separately.

Sodium, the second member of the group, has already been described (Chapter IX).

POTASSIUM, K = 39.

191. Occurrence.—Potassium is the most abundant element of the group. A reference to the table in the Appendix will show that the accessible parts of the earth's crust contain on an average 2.4 per cent of this element. Almost all the common rocks—granite, gneiss, basalt, and so on—contain potassium compounds; and when they break up under the influence of the weather, the potassium compounds pass into the soil, which always contains them. From the soil they are absorbed by plants: potassium is indispensable to vegetable life.

192. **Importance of potassium in the life process.**—Many experiments have shown that the place of the potassium in plants can not be taken by the other metals of the group, for when the attempt is made to displace the potassium by watering the plant systematically with a solution of a lithium compound, for instance, the plant shows signs of poisoning, and finally dies. From the plants potassium finds its way into the bodies of animals, and it is contained in all animal tissues, even in muscular tissue, which does not contain sodium.

193. **History and preparation.**—When a plant is burned, the potassium is left in the ashes as potassium carbonate, K_2CO_3, and this can be separated from the other substances present by treating the ashes with water, in which potassium carbonate dissolves. Wood-ashes were the earliest source of potassium compounds, but they have ceased to be important on account of the discovery of immense deposits of potassium chloride, KCl, at Stassfurt, in Germany.

Potassium was first obtained almost at the same time as sodium by Sir Humphry Davy (p. 68), who decomposed potassium hydroxide, KOH, by the electric current. It is made by heating potassium carbonate to whiteness with powdered charcoal:

$$K_2CO_3 + 2C = 3CO + 2K.$$
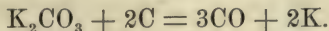
Potassium is liberated as a green vapor, which is condensed under petroleum. The process is dangerous and explosions are frequent. Potassium has ceased to be an important product, because sodium, which can be easily and cheaply made by the electric process (p. 68), answers the same purpose in almost all technical operations.

194. **Properties.**—Potassium is a metal, with a silver-white metallic luster which disappears in the air more rapidly than that of sodium. Heated in the air, or in gases containing oxygen, it melts to a mercury-like liquid, which

takes fire and burns with a violet flame to gray *potassium oxide, K_2O,* or to yellow *potassium tetroxide, K_2O_4,* or to a mixture of both, according to the temperature and the amount of oxygen supplied to it. It decomposes water energetically, thus:

$$K + H_2O = KOH + H,$$
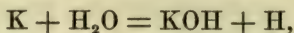
and the hydrogen evolved catches fire at once, burning with a flame colored violet by potassium.

195. Potassium hydroxide, KOH, commonly called caustic potash, was formerly made in the same way as sodium hydroxide (p. 70), by boiling potassium carbonate with slaked lime:

$$Ca(OH)_2 + K_2CO_3 = CaCO_3 + 2KOH.$$
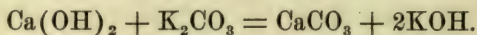
At present it is prepared by passing the electric current through a solution of potassium chloride. This solution contains $\overset{+}{K}$ ions positively charged and $\overset{-}{Cl}$ ions charged negatively. When the current passes the chlorine ions proceed to the positive pole, give up their charges, and are liberated as chlorine gas, which is used for the manufacture of bleaching-powder (p. 88). The potassium ions go to the negative pole, but of course a metal like potassium can not be set free in the presence of water. Instead, hydrogen is liberated from the water. This leaves hydroxyl ions; and since the liquid around the negative pole contains potassium ions also, it is simply a solution of potassium hydroxide, which can be obtained solid by evaporation. Chlorine and potassium hydroxide act upon each other chemically (p. 87), and therefore it is necessary to keep them apart. This is accomplished by placing between the positive and negative poles a porous partition, which allows the current to pass, but does not permit the liquids on the two sides to mix.

196. Properties of potassium hydroxide.—Potassium hydroxide is very similar to sodium hydroxide. It usually oc-

curs in commerce in the form of sticks. It is a white solid, melting at a red heat and vaporizing at higher temperatures without decomposition. It is excessively soluble in water, and the solution acts energetically upon vegetable and animal tissues, and possesses in a marked degree all those properties which we have learned to associate with the presence of hydroxyl ions.

197. **Compounds of potassium with sulphur.**—When potassium is gently heated with sulphur, the two combine with explosive energy, and the result is a fused brownish-yellow mass, which may, according to the proportions in which the elements were taken, contain any or all of the following five compounds:

> Potassium monosulphide, K_2S;
>   "   disulphide, K_2S_2;
>   "   trisulphide, K_2S_3;
>   "   tetrasulphide, K_2S_4;
>   "   pentasulphide, K_2S_5.

It is not possible to obtain any of these compounds in the pure state by heating the two elements together, but they have all been prepared by other methods. They are yellow or red solids, soluble in water.

Sulphur in the sulphides has a combining power equal to that of two hydrogen atoms. This is shown, for example, in hydrogen sulphide, H_2S. This we express by the statement that sulphur in these compounds has a valence of two, or is *bivalent*. We have seen that the metals of the sodium group are usually univalent. The composition of potassium monosulphide is just what we should expect. We may think of it as hydrogen sulphide, H_2S, in which each hydrogen atom has been replaced by an atom of potassium—

> H_2S, hydrogen sulphide;
> K_2S, potassium sulphide;

and in it the potassium is univalent, the sulphur bivalent. But what are we to think of the other compounds—of K_2S_2, for instance? If each sulphur atom is bivalent in this substance, the two must have a combining power of four; and since it only requires two potassium atoms to combine with them, the potassium must be bivalent. Similar reasoning shows us that if the sulphur is always bivalent, then—

In K_2S_3 the potassium has a valence of three or is *trivalent.*
In K_2S_4 "   "   "   " four " *quadrivalent.*
In K_2S_5 "   "   "   " five " *quinquivalent.*

So that we seem forced to admit that, while potassium is almost always univalent, yet in its compounds with sulphur and in some other compounds—K_2O_4, for instance—it may vary in combining power from one to five.

This conclusion, that the same atom may have different combining powers at different times, is unpleasant to some chemists. Here is a way of escape from it. Let us admit that in K_2S_2 the sulphur atoms are united together, and each holds a potassium atom, thus:

$$K—S—S—K,$$
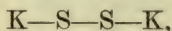
then we can write a formula for the compound and still believe that the potassium is univalent. In the same way potassium trisulphide, K_2S_3, can be written—

$$K—S—S—S—K;$$
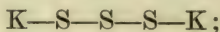
potassium tetrasulphide, K_2S_4—

$$K—S—S—S—S—K;$$
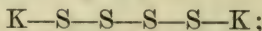
and potassium pentasulphide, K_2S_5—

$$K—S—S—S—S—S—K.$$
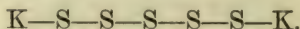
Formulas like these, which express our belief regarding the way in which the atoms are united in compounds, are called *structural* formulas. The structural formulas of these compounds of potassium and sulphur are of no im-

portance, because there is no experimental evidence in their favor. But the student should carefully notice the important idea that it is possible to think of the molecule of a compound as a structure in which the atoms have a perfectly definite arrangement. This "doctrine of chemical structure," as it is called, has been of priceless value in dealing with the innumerable compounds which carbon forms with other elements.

198. **Potassium chloride, KCl.** — When potassium is heated gently in chlorine, it burns with a violet-red flame to potassium chloride, KCl. This compound occurs in great quantities at Stassfurt, in Germany, and it is the raw material for the manufacture of all potassium compounds. Potassium chloride strongly resembles sodium chloride. It is colorless when pure and crystallizes in cubes. It is quite soluble in water. Its taste resembles that of salt, but is sharper. The fact that it takes the place of salt in the diet of certain savages has been referred to (p. 67).

199. *Potassium bromide*, KBr, and *potassium iodide*, KI, are white, crystallize usually in cubes, and are readily soluble in water. They are extensively used in medicine and, especially the first, in photography.

CHAPTER XIX

THE COPPER GROUP

Copper, Cu.   **Silver, Ag.**   **Gold, Au.**

200. **General properties.**—The metals of this group are
not so strongly metallic, chemically, as the metals of the
sodium group. Silver and gold are not affected by water
or by oxygen at any temperature, nor is copper affected by
either in the cold. Oxygen, however, combines with heated
copper, and when steam is led over melted copper at a white
heat, copper oxide is formed and hydrogen liberated, but
very slowly.

This indifference toward water and oxygen explains the
fact that these metals occur free in nature, and therefore
became known to man very early, while the elements of the
sodium group have all been discovered within the last hun-
dred years. The elements of the sodium group are not
employed for any of the purposes which we associate with
metals, for their conduct toward air and water forbids it.
But the elements of the copper group are particularly
adapted to such uses—for coinage, for example.

Although copper, silver, and gold are far less metallic
chemically than the sodium group, they possess the physical
properties of a metal to a much greater extent.

Copper, silver, and gold greatly surpass sodium and its
allies in tenacity, malleability, and ductility. In this group
tenacity decreases with increasing atomic weight, copper
being the most tenacious. With malleability and ductility
the reverse is true, gold being by far the most malleable and

ductile. All three are excellent conductors of heat and of the electric current. They are far denser than the elements of the sodium group—copper, the lightest, being about nine times as dense as water—and melt at higher temperatures, at a bright yellow heat or beyond.

COPPER, $Cu = 63.5$.

201. **Occurrence.**—Copper is widely distributed in nature. The most important copper-mining districts are in Montana, Arizona, and Michigan, where great quantities of it are mined. Many compounds of the metal—for instance, the oxide Cu_2O and the sulphide Cu_2S—are abundant enough to be important as ores. Traces of copper occur in many plants—hops always contain it—and in the animal kingdom also—for example, in the red feathers of certain birds and in the human kidneys.

202. **Physical properties.**—Pure copper has a rose-red color, different from that of ordinary copper. It is very ductile, malleable, and tenacious, and its ability to conduct heat and the electric current is greater than that of any other metal except silver. It melts at a yellow heat, and at the high temperature of the electric arc (3500°) it rapidly boils away, torrents of brown smoke being produced by the combination of the vapor to CuO, with the oxygen of the air.

203. **Chemical properties.**—When a compact piece of copper is heated in the air it combines slowly with oxygen. Two oxides are produced. Next the copper is red cuprous oxide, Cu_2O, and outside a black coating of cupric oxide, CuO. At a white heat melted copper burns in the air with a green light to cupric oxide, and slowly takes the oxygen from steam led over it, thus:

$$H_2O + Cu = CuO + H_2.$$
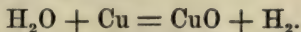
Air and water at ordinary temperatures affect it very little, but in moist air containing carbon dioxide it becomes cov-

ered with a green film which contains the hydroxide and the carbonate, $Cu(OH)_2CuCO_3$. This coating is called verdigris. Copper is hardly affected by hydrochloric acid; sulphuric acid, when strong and hot, attacks it rapidly, and nitric acid, even dilute and cold, quickly dissolves it.

204. **Action upon the body.**—Copper and copper compounds are not very poisonous, and when they are taken into the system daily through long periods, the metal does not accumulate in the body and finally produce poisoning, as lead does, but is excreted as fast as introduced.

205. **Uses.**—Copper is an important metal practically. Large quantities of it are made into wires for the purpose of conducting the electric current, and it makes part of many important alloys, like brass, which is an alloy of copper and zinc, and bronze, an alloy of copper and tin.

206. **Compounds of copper and oxygen.**—Six compounds of these two elements are known, of which only two are important enough to be discussed here. These are cuprous oxide, Cu_2O, and cupric oxide, CuO.

It will be noticed that if oxygen is bivalent, then in cupric oxide the copper is bivalent. The compound can be viewed as water in which the two hydrogen atoms are replaced by an atom of copper:

$$H_2O \qquad CuO.$$
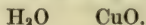
With cuprous oxide there are two possibilities. We can write it

$$\begin{matrix} Cu \\ Cu \end{matrix} \Big> O,$$

in which case it is water in which two hydrogen atoms are replaced by two atoms of copper, and the copper is univalent. Or we can consider that the copper atoms are combined together and also with oxygen—

$$\begin{matrix} Cu \\ | \\ Cu \end{matrix} \Big> O;$$

and in this case the copper will be bivalent, just as it is in cupric oxide. Now, so far as the oxides are concerned, there is no evidence in favor of either formula. But corresponding to each oxide is a

whole series of compounds. Thus hydrochloric acid converts cupric oxide into cupric chloride, $CuCl_2$—

$$CuO + 2HCl = CuCl_2 + H_2O—$$
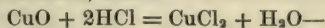
and cuprous oxide into cuprous chloride, Cu_2Cl_2—

$$Cu_2O + 2HCl = Cu_2Cl_2 + H_2O.$$

The *composition* of cuprous chloride would be equally well described by the formula CuCl, but it has been converted into vapor, and the density of this vapor is 99.1 referred to hydrogen. This shows (Chapter XVI) that the molecular weight must be 99.1×2, or 198.2, and therefore we must write the formula Cu_2Cl_2—not CuCl—and the atoms must be arranged thus:

$$\begin{array}{l} Cu—Cl \\ | \\ Cu—Cl. \end{array}$$

It is convenient to think that all of the cuprous compounds contain a pair of bivalent copper atoms linked together, the remaining two valences being used to hold the other elements of the compound,

$$\begin{array}{l} Cu— \\ | \\ Cu—. \end{array}$$

207. Cuprous oxide, Cu_2O, occurs in nature, and is called *red copper ore*. It can be made by heating a mixture of cupric oxide and finely divided copper, air being excluded:

$$Cu + CuO = Cu_2O.$$
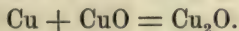
It is a carmine-red powder insoluble in water. As we have seen above, hydrochloric acid converts it into white cuprous chloride. But when it is treated with sulphuric acid, the color changes to the rose-red of metallic copper and blue *cupric* sulphate dissolves, thus:

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O.$$
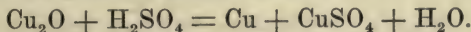
Most acids behave like sulphuric acid, converting it into a cupric salt, which dissolves, and copper, which remains.

208. **Cupric oxide**, CuO, commonly called copper oxide, can be obtained by heating copper for a long time to redness in the air, or by heating cupric nitrate—

$$Cu(NO_3)_2 = CuO + 2NO_2 + O,$$
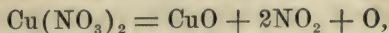
the reaction being similar to that which occurs when **lead**

11

nitrate is heated (p. 113). It is a black powder, insoluble in water but soluble in acids, with which it forms blue cupric salts:

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$
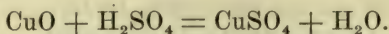
When cupric oxide is heated alone, it does not readily yield up its oxygen. It requires the high temperature of the electric arc to decompose it completely into oxygen and copper. But when heated with hydrogen or with carbon, its oxygen is easily removed, producing water or carbon dioxide:

$$CuO + H_2 = Cu + H_2O$$
$$2CuO + C = 2Cu + CO_2.$$
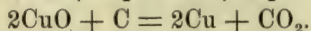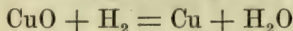
Cupric oxide is much employed by chemists in the analysis of compounds containing carbon and hydrogen, for on being heated with them in a glass tube it converts their hydrogen into water and their carbon into carbon dioxide, both of which are easily collected separately and weighed. From these two weights the percentages of hydrogen and of carbon in the substance heated can be calculated.

209. Cuprous compounds.—These all contain the linked pair of copper atoms, $\begin{matrix} Cu \\ | \\ Cu \end{matrix}$ They are almost all insoluble in water, and colorless.

Cuprous chloride, Cu_2Cl_2, can be made by shaking a solution of cupric chloride, $CuCl_2$, with copper filings. It is a white crystalline powder insoluble in water. It darkens on exposure to light, and has many points of resemblance with silver chloride, $AgCl$. The fact that the density of its vapor shows that the formula is Cu_2Cl_2, not $CuCl$, has been noticed.

Cuprous bromide, Cu_2Br_2, and cuprous iodide, Cu_2I_2, are also insoluble in water and decomposed by light. They are similar to silver bromide and silver iodide.

210. Cupric compounds.—All cupric compounds—for example, cupric chloride, $CuCl_2$—contain one bivalent cop-

per atom. When they are dissolved in water this atom be-
comes an ion with a double positive charge. Thus, cupric
chloride in dilute water solution separates into three ions—
$\overset{++}{Cu}$, $\overset{-}{Cl}$, and $\overset{-}{Cl}$. This cupric ion communicates a blue color
to all solutions of cupric salts, and the color of dilute water
solutions of cupric salts is the same *no matter what the dis-
solved salt was,* not only the same on simply looking at the
liquid, but the same also when light which has passed
through the liquid is sorted out into its colors by means of
a prism. This is an interesting proof that the dissolved
salts have separated into ions, for otherwise different salts
would give different colors to their solutions. This remark
applies not only to the cupric salts but to all metallic salts
whose water solutions are colored (p. 131).

211. **Different series of salts of the same metal.**—This is
the first time we have had an opportunity to notice a re-
markable fact—the fact that many metals form *two differ-
ent series of salts,* the two sets differing greatly in their
properties. Solutions of the cuprous salts are just as un-
like those of the cupric salts in color and in chemical con-
duct as though they contained some other metal, and this

shows us that the cuprous ion, $\overset{+}{\underset{+}{\underset{Cu}{\overset{Cu}{|}}}}$ and the cupric ion, $\overset{++}{Cu}$,

are very different things, and communicate very different
properties to liquids containing them, yet both are nothing
but copper. This reminds us of ordinary oxygen and ozone,
two substances composed of the same element and yet very
unlike.

It will be seen that in a cupric ion, $\overset{++}{Cu}$, one atom of
copper carries just the same electric charge as is carried

by two atoms in the cuprous ion, $\overset{+}{\underset{+}{\underset{Cu}{\overset{Cu}{|}}}}$ Therefore, if we

allow the same current to pass through a cuprous and a cupric solution, the amount of copper precipitated in an hour will be twice as great in the cuprous solution as in the cupric.

212. **Reaction of cupric compounds with metals.**—When zinc or iron is placed in a solution of a salt of copper, the metal dissolves and copper appears in its place. Thus, if a penknife-blade is dipped into a solution of cupric chloride, it becomes covered at once with red metallic copper. This was regarded in the middle ages as a transformation of iron into copper. We can write the reaction—

$$Fe + CuCl_2 = FeCl_2 + Cu.$$
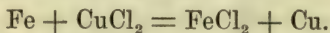
But the solution of cupric chloride consists of ions $\overset{++}{Cu}$, $\overset{-}{Cl}$, and $\overset{-}{Cl}$, and it is clear that the chlorine ions take no part in the process. What happens is simply this. An iron atom robs a copper ion of its charge and takes its place in the liquid, the copper separating as metal, thus:

$$Fe + \overset{++}{Cu} = \overset{++}{Fe} + Cu.$$
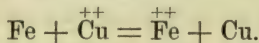
Since the liquid already contained chlorine ions, and now contains iron ions, it becomes a solution of iron chloride, $FeCl_2$.

213. **Cupric chloride,** $CuCl_2$, can be obtained by burning copper in chlorine, or by dissolving cupric oxide in hydrochloric acid, when it crystallizes in green deliquescent needles of the composition $CuCl_2 2H_2O$, which are very soluble in water. The strong solution of cupric chloride is grass-green, because the salt is nearly all present as molecules $CuCl_2$, not separated into ions. In all solutions the amount of the salt which is so separated increases rapidly when the liquid is diluted, and when water is added to a solution of cupric chloride there is a plain change from the bright green of $CuCl_2$ to the blue color of the cupric ion $\overset{++}{Cu}$.

Cupric bromide, $CuBr_2$, is similar to the chloride. The student should notice how different these substances are from the corresponding cuprous compounds.

Cupric iodide, CuI_2, does not exist. Various reactions by which we should expect it to be formed yield instead a mixture of cuprous iodide and iodine:

$$2CuI_2 = Cu_2I_2 + I_2.$$
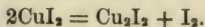
214. **Cupric sulphate**, $CuSO_4$, is the most important cupric salt. It can be made by treating copper with strong sulphuric acid or by heating copper sulphide gently in a current of air, when it takes up oxygen. It is a white powder, which when thrown into water dissolves, with evolution of much heat, to a blue liquid. When this solution is evaporated, blue crystals of the composition $CuSO_4 5H_2O$ are deposited. These crystals are called "bluestone" or "blue vitriol." Large quantities of bluestone are employed in copper-plating and in filling electric batteries, and the water solution is much used in agriculture for the destruction of parasites upon plants.

CHAPTER XX

SILVER, Ag = 108.

215. Occurrence and extraction.—Metallic silver occurs in nature, and is of some importance as an ore. The chloride AgCl—called horn-silver—and the sulphide Ag_2S are important silver ores. Silver is very commonly associated with lead, and most lead ores contain a little silver, very often enough to pay for its extraction. This is done at present by melting the lead obtained from such ores and adding to it 2 to 3 per cent of zinc and stirring thoroughly. When the vessel is allowed to stand there rises to the surface a layer which consists of an alloy of zinc, lead, and silver. This is removed, and the lower layer—mainly lead—is treated again with zinc in order to extract the last traces of silver.

The alloy of zinc, lead, and silver is distilled, when the zinc is driven off as vapor, condensed, and used again. An alloy of lead very rich in silver remains, and the silver is extracted from this by *cupellation*. This consists in melting the alloy in a vessel lined with bone-ash, a current of air being drawn over the surface. The lead is converted into lead oxide, PbO, which is partly vaporized and partly absorbed by the bone-ash. When the amount of lead becomes small, brilliant rainbow hues play over the surface of the melted mass, and finally the bright surface of the silver beneath appears. Then the process is stopped.

152

216. Properties.—Silver is a lustrous, white metal which is very ductile and malleable, and a better conductor of heat and the electric current than any other substance. It melts at a clear yellow heat ($1000°$) and vaporizes at higher temperatures. It can easily be distilled in the oxyhydrogen flame, in lime vessels, and this method has been employed in the preparation of the pure metal. Stas, when he needed pure silver to determine the atomic weight of the metal, obtained it in this way. He informs us that the vapor is pale blue, and that some of it escaped into the air, making it turbid and giving it a metallic taste.

Silver is somewhat sensitive to light, and when a glass plate is thinly coated with it and exposed in a camera a picture can be obtained. This shows that there must be at least two allotropic forms of the metal, one of which is formed by the action of light on the other, and, in fact, a number of modifications of silver have been described.

Silver is not affected by water or by oxygen at any temperature. We have seen that ozone acts upon it, converting the surface into black Ag_2O_2. A silver plate exposed near an oxyhydrogen flame is blackened because ozone is formed from the oxygen by the high temperature and then acts upon the silver. The tarnishing of silver vessels in the air may occasionally be due to the action of ozone, but it is usually owing to the production of a film of silver sulphide, Ag_2S, for there is always a little sulphur in coal, and therefore the air of a house always contains traces of gases containing sulphur, which come from the burning of coal and of ordinary gas, which is made from it. In shops the tarnish is prevented by keeping the silver in closed cases, with a dish containing a little lime, which is renewed from time to time.

Silver is scarcely acted upon by hydrochloric or dilute sulphuric acid. Strong sulphuric acid converts it into silver sulphate, Ag_2SO_4, and nitric acid readily dissolves it to

silver nitrate, $AgNO_3$. Silver may be regarded as *univalent* in all its compounds.

217. Compounds of silver with oxygen.—Two oxides of silver are known with certainty.

Silver oxide, Ag_2O, is a brown powder, easily decomposed by heat into silver and oxygen. It is very slightly soluble in water, and the solution has an unpleasant metallic taste and distinct basic properties. It must therefore contain hydroxyl ions, $\overset{-}{OH}$, and silver ions, $\overset{+}{Ag}$, or, what is the same thing, it must be a solution of silver hydroxide, AgOH. But this substance has never been obtained solid. Reactions by which we should expect it to be produced always yield instead silver oxide and water, thus:

$$2AgOH = Ag_2O + H_2O.$$
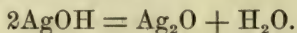
Silver dioxide, Ag_2O_2, which we may write Ag—O—O—Ag, has been obtained by the action of ozone on silver and by other methods. It crystallizes in black needles, which are insoluble in water and easily decomposed by heat.

218. *Silver sulphide,* Ag_2S, can be obtained in blackish-gray crystals by heating finely divided silver in the vapor of sulphur. *Oxidized silver* is a misleading name given to silver which has been thinly coated with silver sulphide by boiling it in a solution containing potassium pentasulphide, K_2S_5.

219. Compounds of silver with fluorine, chlorine, bromine, and iodine.—These four elements closely resemble each other chemically, and it is convenient to consider their silver compounds together.

Silver fluoride, AgF, differs remarkably from the other three compounds. It is a clear yellow, horny mass, which turns black in the light, is deliquescent, and very soluble in water. When silver is suspended in this solution a beautifully crystallized salt, called silver subfluoride, Ag_2F, is produced.

It has been pointed out that complete insolubility is a state of
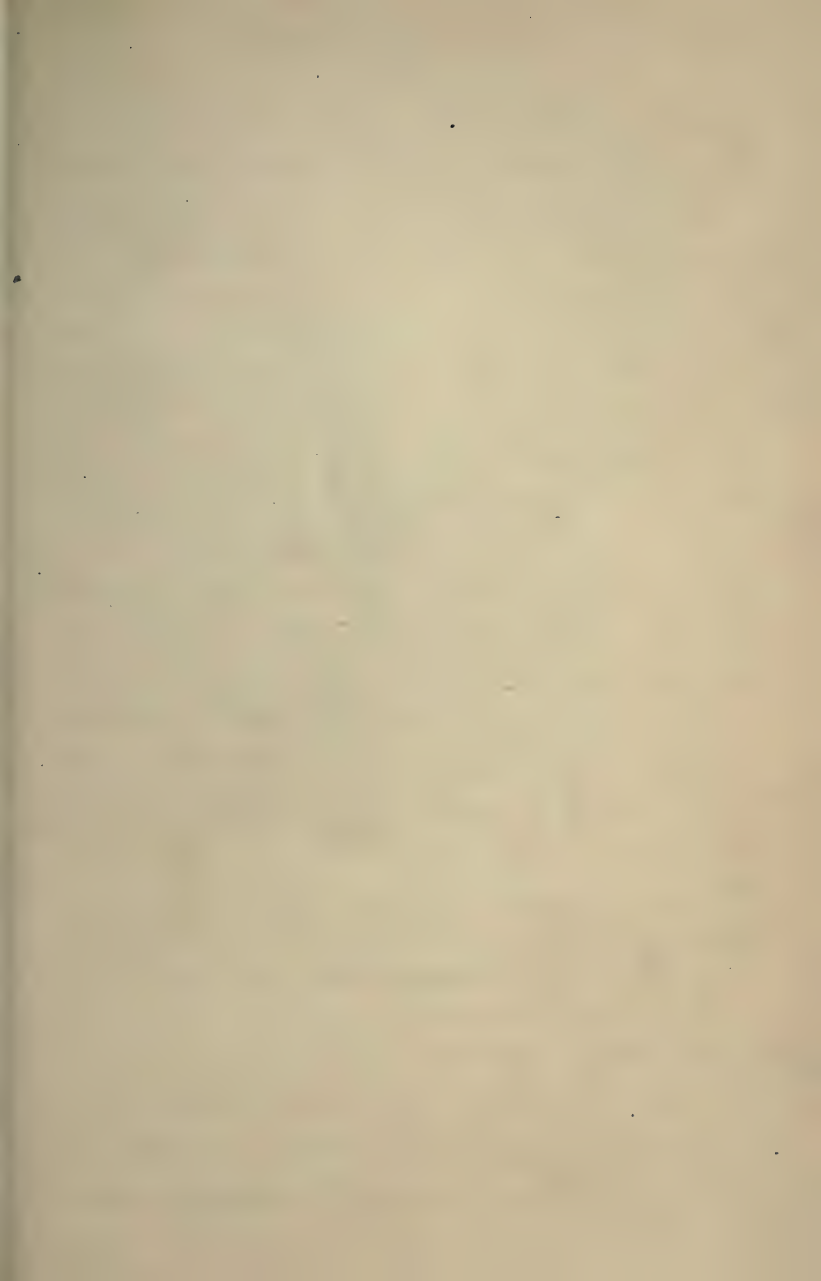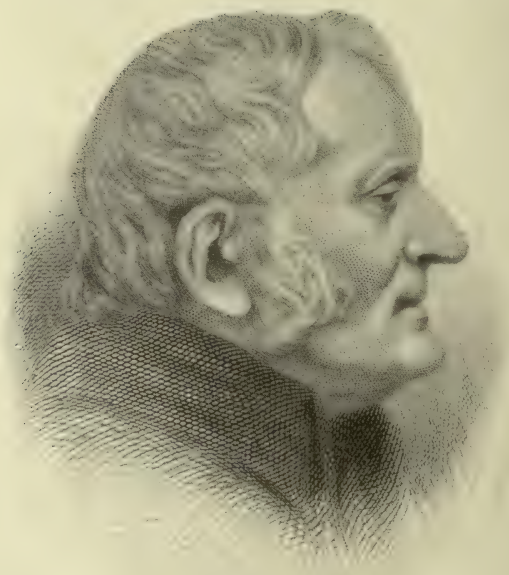
JOHN DALTON

B. England, 1766.   D. 1844.

things which real substances approach but probably never reach. Silver chloride, bromide, and iodide are interesting examples of this fact. It takes something like a million parts of water to dissolve one part of silver chloride, and the others are still less soluble, yet it has been shown that water dissolves small quantities of all of them, and that the solubility decreases in the order in which the compounds have been named.

220. **Silver chloride**, AgCl, separates as a heavy, white, curdy precipitate when a liquid containing chlorine ions is mixed with one containing silver ions:

$$\overset{+}{Ag} + \overset{-}{Cl} = AgCl.$$
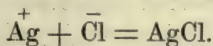
Thus, when a solution of table salt is mixed with a solution of silver nitrate:

$$NaCl + AgNO_3 = AgCl + NaNO_3.$$
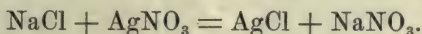
Silver chloride turns bluish-gray, and finally black, when exposed to light. This is important in photography, and has been known for more than a century, yet we are still uncertain with respect to what happens when the darkening occurs.

Silver bromide, AgBr, and silver iodide, AgI, resemble silver chloride. They are yellow, and like the chloride, darken when exposed to light.

PHOTOGRAPHY

221. **The daguerreotype process.**—The sensitiveness of these three silver compounds to light is the basis of the photographic process. The first attempt to apply the fact to picture-making which attained any practical importance was that of *Daguerre*. He coated a silver plate with a film of silver iodide by allowing the vapor of iodine to act upon it, and then exposed the sensitive surface so obtained in a camera; but the exposure required was long and the results unsatisfactory until he discovered, quite by accident, that if, after the exposure, the plate was treated with the vapor

of mercury, the mercury would condense upon those parts of the surface which had been acted upon by the light, and the picture appear. Then the plate was treated with a liquid which would dissolve away the unaltered silver iodide from those portions upon which the light had not acted. This was necessary, because otherwise the plate would have blackened uniformly on exposure to light, destroying the picture.

222. *The modern dry plate* consists of a plate of glass, one side of which is covered with a film of hardened gelatin containing finely divided silver bromide, AgBr. This is placed in the camera in such a way that this surface is in the focus of the lens, and receives the image. After the exposure to light the plate is just the same in appearance as before. It is only on being treated with a liquid called the "developer" that the picture makes its appearance. A developer is a substance which has this peculiar property, that while it has no action upon silver bromide which has been kept in the dark, it converts silver bromide which has been exposed to light into metallic silver. Accordingly, silver bromide which has been exposed to light must have sustained some alteration which causes it to be attacked by the developer afterward. In spite of much careful work upon the problem, the nature of this change is still disputed. This much is known, that bromine is set free when light acts upon silver bromide. Perhaps the light decomposes very small quantities of the silver bromide into silver and bromine, leaving traces of finely divided silver wherever it acts upon the plate. Then, in the developing process, the silver produced by the action of the developer on the silver bromide of the plate crystallizes upon these silver particles, just as a supersaturated solution crystallizes upon a particle of the same substance thrown into it (p. 14). If this view is correct, the quantity of silver produced must be very small, for when a plate is exposed to light, and then the silver

bromide dissolved out of it without any developing, no silver can be detected even under the microscope.

Or perhaps the light converts the silver bromide into silver sub-bromide, Ag_2Br (analogous to silver sub-fluoride, Ag_2F), which is then converted into silver by the developer.

223. At any rate, wherever the light has fallen upon the plate, the developer produces dark metallic silver. The next step is to dissolve away the unaltered silver bromide in order to prevent it from being acted upon by light and spoiling the image. This is called "*fixing*," and is accom-
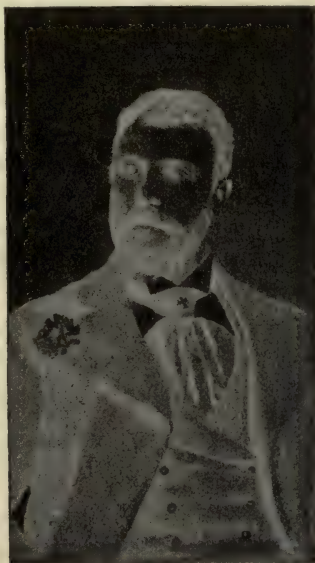
Fig. 34, *a.*—Positive.　　Fig. 34, *b.*—Negative.

plished by soaking the plate in a solution of *sodium thiosulphate*, $Na_2S_2O_3$, called "*hypo*" by the photographer. The plate is now called a "negative," for the lights and shadows are exactly reversed in it. The bright parts of the image are covered with blackish silver, while the dark portions are simply clear glass (Fig. 34, *b*).

224. After being thoroughly washed and dried the negative is ready for "*printing.*" It is exposed to light, with a piece of sensitive paper back of it, in contact with the image. The light passes easily through the clear portions, which therefore become dark in the print, but is arrested by those parts which are covered with opaque silver, which therefore remain white on the paper. Hence the lights and shadows are again reversed, and are now the same as they were in the original scene.

Various papers are employed for printing. A very common one consists of paper covered with a film of albumin or gelatin containing silver chloride, $AgCl$. We have seen that silver chloride darkens when it is exposed to light. There is still doubt as to what happens to it when it is alone, but in presence of the albumin silver is produced. Silver obtained in this way has an unpleasant reddish color, so the paper is afterward dipped in a solution containing gold chloride. In this way part of the silver of the image is replaced by gold, which gives a more satisfactory color. This is called *toning.*

The "developing" papers, like "Velox," work on the same principle as a plate. The paper is covered with a film of gelatin containing silver bromide, and when it is exposed back of a negative the paper remains white, but the picture appears upon dipping the paper into the developer.

Both these kinds of paper require to be "fixed" after the picture appears. In other words, the unaltered silver chloride, or silver bromide, as the case may be, must be removed, since otherwise the whole paper would shortly turn black. This is accomplished in just the same way as with the plate, by soaking the paper in a solution of sodium thiosulphate and washing thoroughly.

CHAPTER XXI

THE COPPER GROUP (Continued)

GOLD, Au = 197.

225. Occurrence and extraction.—Gold occurs free in nature, and was therefore among the earliest metals known to man. It is rather widely distributed, but is found abundantly in only a few localities. The great gold deposits are in South Africa, Australia, the United States, and Russia. Under ordinary circumstances South Africa stands first as regards the amount of gold produced, though of late the interruption of mining by war in the Transvaal has allowed the United States to take first rank.

Gold occurs chiefly in two ways, either in grains or fragments scattered through beds of gravel or sand (placer deposits), or else disseminated through some compact rock, usually quartz. In working a placer deposit on a large scale a powerful jet of water is thrown into the mass. A torrent of water charged with earth and stones rushes out, and is led away through a long inclined channel built of boards. Pieces of wood projecting above the general level are nailed transversely across the bottom of this channel at intervals. The gold, being far denser than the rest of the solid matter carried by the water, sinks most rapidly and collects back of these projections. From time to time the water is stopped and the gold removed.

A compact rock containing gold is crushed finely and then brought into contact with mercury. Gold forms an alloy—an amalgam, as it is called—with mercury more

readily than any other metal. This amalgam is removed and distilled. The mercury vaporizes and is condensed, while the gold remains and is further purified.

226. Properties.—Gold is a metal with a characteristic yellow color and, when polished, a brilliant luster. It has a very low specific heat, and therefore feels warmer to the hand than copper or iron at the same temperature. It is marvelously malleable and ductile. Gold is harder than tin but softer than silver, and an object made of it would wear away rapidly in use. Therefore the gold for use in coinage is alloyed with 10 per cent of copper, and jeweler's gold with copper or copper and silver.

When heated, gold melts at a somewhat higher temperature than silver, and at the temperature of the electric arc vaporizes rapidly, torrents of greenish-yellow smoke emerging from the vessel. It is not affected by oxygen, by water, or by air at any temperature, nor is it attacked by the ordinary acids. It is said that finely divided gold dissolves in very strong nitric acid, and is precipitated again when water is added. Although compact gold is not affected by either hydrochloric or nitric acids it dissolves readily in the mixture of the two. This mixture is called "aqua regia," and it also dissolves platinum and some other metals which are not attacked by either acid alone. This is because the nitric acid liberates chlorine from the hydrochloric acid, and the chlorine converts the metal into its chloride.

227. Uses.—On account of its appearance and its resistance to the atmosphere, gold is extensively used for plating other metals. The object to be gilded is thinly covered with gold amalgam [1] and then carefully heated to drive off the mercury. Or the object is suspended in a solution con-

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[1] The alloys of mercury with other metals are called *amalgams*.

taining gold and made the negative pole of a feeble current passing through the liquid. The first method is called "fire-gilding" and the second "electro-plating," and by either an exceedingly thin film of gold can be deposited.

228. Gold can be either univalent or trivalent. The compounds in which it is univalent—the aurous compounds—are much like the compounds of silver. Thus, aurous chloride, $AuCl$, aurous bromide, $AuBr$, and aurous iodide, AuI, are white or yellow, and insoluble in water. *They are easily decomposed by heat, leaving a residue of gold, and this, in fact, is true of all gold compounds without exception.*

229. The compounds in which gold is trivalent, the *auric compounds,* are the most important.

Auric oxide, Au_2O_3, is a blackish-brown powder, which at 250° separates into gold and oxygen.[1] When ammonia water is poured over it, it is converted into "*fulminating gold,*" a green powder which explodes most violently on being heated or struck.

Auric hydroxide, $Au(OH)_3$, is a yellow powder insoluble in water. At 100° water separates from it and auric oxide remains:

$$2Au(OH)_3 = Au_2O_3 + 3H_2O.$$
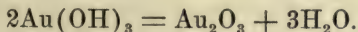
Auric hydroxide behaves more like an acid than a base. Its hydrogen can be replaced by metals like sodium and potassium, forming salts called aurates. This shows that, while gold is a perfect metal physically, its metallic character chemically is not well marked.

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[1] In statements like this it is understood that the substance is heated in the air. The temperature at which auric oxide will yield up its oxygen depends entirely upon the atmosphere in which it is heated. Thus, if sealed up in a strong glass tube with compressed oxygen, a higher temperature than 250° would be needed to decompose it, while, on the other hand, when it is heated in a vacuum, the temperature required is not so high as in the air. The more free oxygen in the gas in contact with it the higher the temperature required.

Auric chloride, $AuCl_3$, is made by dissolving gold in aqua regia, or better, by treating finely divided gold with chlorine and dissolving the product in water, which is then evaporated. Auric chloride forms brown, imperfect crystals freely soluble in water. Heat separates it into gold and chlorine.
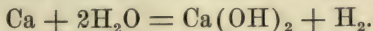
CHAPTER XXII

THE CALCIUM GROUP

Calcium, Ca.   Strontium, Sr.   Barium, Ba.

230. General properties of the calcium group.—Calcium, strontium, and barium are strongly metallic. They oxidize rapidly in the air, and decompose water energetically, producing their hydroxides and liberating hydrogen, thus:

$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

The hydroxides are very strong bases, barium hydroxide being the strongest.

It will be noticed that there is a considerable similarity between these metals and the metals of the sodium group. The most important difference is that these metals are almost always bivalent, and this will enable us to write the formulas of most of their compounds without memorizing them.

CALCIUM, Ca = 40.

231. Occurrence.—Calcium stands fifth among the elements in point of abundance, making up nearly 4 per cent of the earth's crust. Limestone and chalk are calcium carbonate, $CaCO_3$, and marble is the same material in compact crystalline state. The *pearl* is also calcium carbonate, and owes its value to its beautiful luster, not to the material of which it consists. Most shells—those of oysters and clams, for instance—consist of calcium carbonate with more or less organic matter.[1] Compounds of calcium are con-

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[1] By organic matter we mean complicated compounds of carbon, hydrogen, nitrogen, and oxygen, originating in organized beings—

tained in most common rocks, in all soils, and in the bodies of most plants and animals. In the latter it exists chiefly in the bones and teeth, which contain about half their weight of *calcium phosphate,* $Ca_3(PO_4)_2$, the rest being mainly organic matter. When bones are burned, the organic matter is consumed and the calcium phosphate is left as an ash.

232. **Preparation and properties.**—Compounds of calcium, like calcium carbonate and lime—which is calcium oxide, CaO—have been known for centuries, but the metal has only been obtained pure and in large quantities quite recently (1898). This was accomplished by heating calcium iodide, CaI_2, to redness with sodium in a crucible:

$$CaI_2 + 2Na = 2NaI + Ca.$$
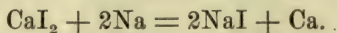
When the mass cools it is powdered and treated with pure alcohol, which dissolves the sodium iodide, leaving the calcium as a gray powder, which can be made into a compact mass by melting it in a vacuum.

Calcium is a silver-white metal with a brilliant luster, which it rapidly loses in moist air. It is somewhat harder than lead, and less than twice as dense as water. Heated in a vacuum, it melts at a red heat. Heated in oxygen, it takes fire and burns with blinding brilliancy to lime—calcium oxide, CaO—and the temperature produced is so high that the lime melts. When calcium is burned in the air it combines not only with the oxygen but also with the nitrogen, and the product is a mixture of lime with calcium nitride, Ca_3N_2. When calcium is thrown into water hydrogen quickly escapes and a white mass of *calcium hydroxide,* $Ca(OH)_2$—commonly called "slaked lime"—is formed.

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animals or plants. Albumin and gelatin are examples. The chemical nature of such substances is not yet fully understood.

233. Calcium oxide, CaO (lime), is the product of the burning of calcium in oxygen. Lime is made on the large scale by heating some form of calcium carbonate in such a way that the carbon dioxide produced can readily escape:

$$CaCO_3 = CaO + CO_2.$$
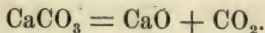
Oyster-shells, limestone, or marble is mixed with coal and thrown in at the top of a furnace—the lime-kiln—the lime produced being removed at the bottom and new materials supplied above so that the process is continuous. Cases of suffocation sometimes occur during the winter among people who, attracted by the warmth, attempt to sleep near a lime-kiln, and the equation above helps us to understand this, for carbon dioxide, CO_2, is a suffocating gas.

If calcium carbonate, $CaCO_3$, is heated in a closed vessel *which it completely fills*, it can be melted without this decomposition occurring. If the calcium carbonate only partly fills the vessel in which it is heated, some lime will be produced, and carbon dioxide will accumulate in the space above the solid. The bottom of the vessel will contain a solid mixture of lime and calcium carbonate, and above this there will be a space containing gaseous carbon dioxide. The weight of carbon dioxide in each cubic centimeter of this space, or, what is exactly the same thing, the pressure of the gas against the walls of the vessel, depends entirely upon the temperature, and is not in the least affected by the size of the vessel nor by the quantity of lime or calcium carbonate in it. For every temperature the pressure of the carbon dioxide against the vessel walls—or the quantity of the gas in each cubic centimeter—has a certain value, and when that value has once been reached years of heating to that temperature will not change it nor decompose any more calcium carbonate. The higher the temperature the more calcium carbonate is decomposed and, of course, the greater the pressure. But when calcium carbonate is heated in an open vessel, carbon dioxide constantly escapes, and the decomposition becomes complete. This reminds us of the behavior of water evaporating into an enclosed space; we have seen that water evaporates until the pressure of the water-vapor reaches a value which is always the same at the same temperature. This is a physical change, while the decomposition

of calcium carbonate by heat is a chemical change, yet the two processes have much in common.

Common lime is gray, but the pure substance is white. When treated with the oxyhydrogen flame, it glows brightly —the lime-light—but is not affected otherwise. At the temperature of the electric arc it can readily be melted and boiled. When liquid lime is allowed to cool, it solidifies to a milky crystalline mass, and when a piece of lime is heated for a time, not quite hot enough to melt it, it becomes covered with crystals, which take the form of cubes. Lime, when exposed to the air, slowly absorbs water and carbon dioxide, and falls to a white powder, called " air-slaked lime," which is a mixture of calcium hydroxide and calcium carbonate:

$$CaO + H_2O = Ca(OH)_2$$
$$CaO + CO_2 = CaCO_3.$$
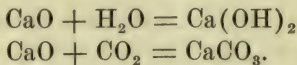
Another compound of calcium and oxygen is known. This is calcium dioxide, CaO_2, which is white and easily separated into lime and oxygen by heat. If we wish to consider calcium as always bivalent—it is certainly *almost* always so—we can write this substance thus:

$$Ca\Big\langle\begin{matrix}O\\ |\\ O.\end{matrix}$$

234. **Calcium hydroxide,** $Ca(OH)_2$, " slaked lime," is made by the union of lime with water. Much heat is produced, and this may be shown by placing on the surface of the lime a little gunpowder, which, if care is taken not to wet it, is inflamed. Calcium hydroxide is a loose white powder, about twice as dense as water, in which it is only slightly soluble. It is one of the very few solids which are more soluble in cold water than in hot. The saturated water solution of calcium hydroxide is called lime-water, and is used in medicine. On account of the small solubility of calcium hydroxide, lime-water contains very little of it, only about one part in seven hundred.

Calcium hydroxide slowly absorbs carbon dioxide from the air, passing into calcium carbonate:
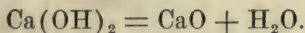
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$
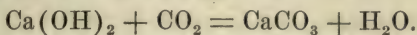
The use of slaked lime for building depends upon this fact. The first hardening of mortar—"setting"—is simple drying. Then follows a slow absorption of carbon dioxide from the air, forming a cement which finally binds the grains of sand together in a mass of stony hardness. This change of calcium hydroxide into calcium carbonate begins at the surface and proceeds very gradually toward the interior, for the examination of ancient samples of mortar—six centuries old or more—has shown that calcium hydroxide is still present in the inner portions.

Lime-water is alkaline to litmus and other indicators, and must therefore contain hydroxyl ions. Calcium hydroxide—like all the hydroxides in this group—is a strong base, reacting with acids to produce calcium salts and water, thus:

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O,$$
$$Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O.[1]$$
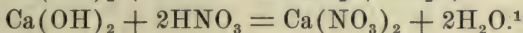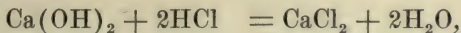
When calcium hydroxide is heated, steam is given off and lime is left:

$$Ca(OH)_2 = CaO + H_2O.$$

235. Compounds of calcium containing sulphur.—*Calcium sulphide,* CaS, is produced when the metal is heated in sulphur vapor, in which it burns brilliantly. It is made by heating a mixture of calcium sulphate and charcoal:

$$CaSO_4 + 2C = CaS + 2CO_2.$$

It is a white solid, very slightly soluble in water. When impure, calcium sulphide possesses the property of being

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[1] The writing of equations like these will become a simple matter for the student if he will remember that calcium is bivalent, and, accordingly, one Ca takes the place of two H.

luminous in the dark after light has acted upon it. It is the basis of *phosphorescent paint*.

Calcium sulphate, $CaSO_4$, occurs in nature as the mineral *anhydrite*. The very common mineral *gypsum* is calcium sulphate with two equivalents of water of crystallization— $CaSO_4, 2H_2O$. When gypsum is gently heated it gives off part of this water and falls to a white powder, which is called " plaster of Paris." If this powder is wet it again combines with the water and sets to a hard mass. In this way plaster casts are made. But if the gypsum is too highly heated in the first place, it will not combine again with water, or only very slowly, and is spoiled for this purpose. It is then said to be " dead-burnt."

Calcium sulphate is not very soluble in water, and separates as a white precipitate when any liquid containing $\overline{\overline{SO}}_4$ ions—for instance, sulphuric acid, or a water solution of any sulphate—is added to a solution containing $\overset{++}{Ca}$ ions (a solution of a calcium salt). When sulphuric acid is added to a strong solution of calcium chloride the liquid solidifies to a white mass:

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl,$$
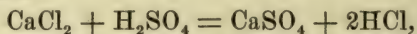
torrents of hydrochloric acid gas being given off.

236. **Calcium fluoride,** CaF_2, is the common mineral *fluorite* usually called *fluorspar*. It crystallizes in cubes, and is transparent and colorless when pure, but, like many other minerals, it is often colored blue, yellow, or some other color by traces of impurities about whose nature there is still dispute. When heated in the dark, the crystals become luminous.

Calcium fluoride is almost insoluble in water. When heated with strong sulphuric acid, it yields calcium sulphate and hydrofluoric acid, HF, and it is employed in the production of this acid—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

237. Calcium chloride, $CaCl_2$, results when calcium burns in chlorine. It is made by dissolving marble in hydrochloric acid:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$
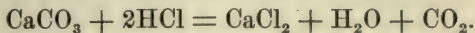
On evaporating and cooling the liquid it separates in colorless crystals, which contain six molecular weights of water, $CaCl_2 6H_2O$. When these are heated, water escapes and anhydrous calcium chloride remains as a white mass. This absorbs water energetically, and it is much used in the laboratory for drying gases and liquids. It is very soluble in water, which dissolves at 100°, about $1\frac{1}{2}$ times its own weight, and much more at higher temperatures.

238. Calcium carbonate, $CaCO_3$, is the most abundant compound of calcium. Compact, not crystalline, and impure, it is *limestone,* one of the most common rocks. From this—probably by the combined action of great pressure, moderately high temperature and water—is formed *marble,* which is a denser, purer variety, composed of a mass of crystals so crowded together that none has had a chance to develop properly. Calcium carbonate in the shape of minute shells pressed together, forming a soft white rock, is called *chalk.* When a grain of sand, or some other small hard particle, gets inside the shell of an oyster, there is deposited around it layer after layer of calcium carbonate, and so is formed the *pearl,* which owes its luster to this structure in layers. The shells of shell-fish consist of calcium carbonate, and the same is true of the coral rock of which coral islands are built up. Stalactites and stalagmites have the same composition. Calcium carbonate, although insoluble in water, dissolves in water containing carbon dioxide. When such a solution oozes from the rocks forming the roof of a cavern, the carbon dioxide escapes into the air and the calcium carbonate, which thereupon

deposits, forms the stalactite, while, at the place where the drip strikes the floor, the stalagmite grows up to meet it.

Calcium compounds which vaporize in the Bunsen flame communicate to it a strong orange color. Compounds like lime, which do not volatilize in the flame, do not color it, but the color can be obtained by first moistening the substance with hydrochloric acid. Calcium chloride is thus produced, and vaporizes when placed in the flame, giving the orange color.

239. Strontium and barium.—These metals are similar to calcium, but are harder and denser. Strontium is yellowish and barium silver white. Both burn brilliantly to their oxides when heated in the air, and both are rapidly converted into their hydroxides by water, thus:

$$Ba + 2H_2O = Ba(OH)_2 + H_2.$$
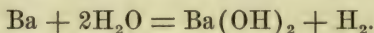
Strontium compounds color the burner-flame red and barium compounds green. *Red fire* is a mixture of strontium nitrate, $Sr(NO_3)_2$, with some combustible substance like powdered sulphur, charcoal, or shellac. The materials are powdered *separately* and carefully mixed. When the mixture is lighted, the combustible material burns at the expense of the oxygen of the nitrate, and the strontium compounds which are carried into the flame produce the red color. *Green fire* is a similar mixture made with barium nitrate instead of the strontium salt.

Barium sulphate, $BaSO_4$, is almost entirely insoluble in water, and is formed as a dense white crystalline precipitate when $\overset{++}{Ba}$ ions and $\overset{--}{SO_4}$ ions are introduced into the same liquid—for instance, when a solution of barium chloride is mixed with dilute sulphuric acid:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl, \text{ or}$$
$$\overset{++}{Ba} + \overset{--}{SO_4} = BaSO_4.$$
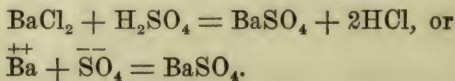
This reaction is much employed as a test for barium, and still more as a test for sulphuric acid and sulphates—that is, for SO_4 ions. Barium sulphate is insoluble in acids and in ammonia, and this aids us to distinguish it from other precipitates of similar appearance.

Radium is a recently discovered metal belonging to the calcium group. Its compounds are rare in nature. They are found chiefly as an impurity in pitchblende (page 232), and even this mineral contains at most one part in a million of radium.

Compounds of radium are luminous in the dark, and the less pure specimens appear to retain their light-giving power for years without loss. They continuously give off heat, and if a tube containing a radium compound is packed in wool, so as to prevent loss of heat, it will maintain itself at a temperature several degrees higher than that of surrounding objects. Radium compounds constantly send out rays which travel in straight lines, and which affect the photographic plate in somewhat the same way as light. However, these rays pass easily through substances which are quite opaque to light, like black paper, aluminium, and copper. They turn glass violet or black, and cause dry air and other non-conducting substances to conduct the electric current. They convert oxygen into ozone and white phosphorus to the red modification. Paper becomes brown and brittle, the green parts of plants lose their coloring matter, and seeds lose their power to germinate under the influence of radium rays. When the skin is subjected to them for a short time there is no apparent effect, but after a week or more the portion which had been exposed becomes red and inflamed, and behaves as though severely burned. The rays have been used with some success for the treatment of cancer and certain skin diseases.

Water which contains a dissolved or suspended radium compound slowly separates into oxygen and hydrogen, just as though an electric current was passing through it, except that the two gases escape *mixed* instead of at different poles.

CHAPTER XXIII

THE ZINC GROUP

**Magnesium,** **Zinc,** **Cadmium,** **Mercury.**

MAGNESIUM, Mg = 24.

240. Occurrence.—Though magnesium itself does not occur in nature, compounds of it are common, and in this form it makes up more than $2\frac{1}{2}$ per cent of the accessible part of the earth's crust, standing sixth among the elements as regards abundance. Magnesium carbonate, $MgCO_3$, is an important mineral, and its double compound with calcium carbonate—dolomite, $CaCO_3MgCO_3$—is very abundant. Asbestos is a magnesium compound, and compounds of magnesium are contained in most common rocks and soils. It is also found in plants, especially in the seeds, and in substances of animal origin, particularly blood, milk, and bones.

241. Preparation and properties.—The first magnesium compound to be obtained was crystallized magnesium sulphate, $MgSO_47H_2O$, which, on account of the mineral spring from whose water it was extracted, is still called " Epsom salts." The metal is best prepared from the chloride, $MgCl_2$, by heating it with sodium:

$$MgCl_2 + 2Na = Mg + 2NaCl,$$
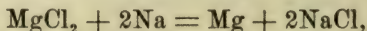
or by fusing it in a crucible and passing the electric current through it, when chlorine is given off and magnesium left, which is purified by distillation.

172

It is a white metal, fairly malleable and ductile, and is scarcely acted upon by air at ordinary temperatures. Heated in the air or in oxygen, it burns with a dazzling bluish-white flame, producing a white smoke of magnesium oxide, MgO. It is doubtful whether magnesium is able to decompose water, but if it does the action is very slow. However, we can easily show that at high temperatures its action upon steam is violent. Some water is placed in a large beaker covered with an asbestos plate having a hole in the center, and the water boiled vigorously until the air has all been expelled from the vessel. Then a piece of burning magnesium wire—held in forceps—is introduced through the orifice into the atmosphere of steam, where it goes on burning more brilliantly than in air. At the same time a pale flame makes its appearance around the orifice in the plate. This is burning hydrogen set free by the combustion of the magnesium in the interior:

$$Mg + H_2O = MgO + H_2.$$
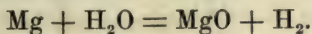
In the same way magnesium is able to burn in most gases and vapors which contain oxygen, combining with the latter and liberating the other constituent. Thus it burns in carbon dioxide, carbon separating as soot. It removes the oxygen from most metallic oxides when mixed with them and heated, and some metals can be obtained in this way which are not easily prepared by other methods.

242. **Uses.**—Magnesium as compact metal has not found much application. An alloy of 10 to 15 per cent of it with aluminium is called *magnalium,* and has valuable properties. It has a silver-white, permanent luster, is very light, and is easily worked and cast. It is used for scales on optical instruments and for the beams of balances. The light of burning magnesium acts rapidly upon the photographic plate, and for this reason the powdered metal is largely used in the production of *flash-light powders.* For this

purpose it is mixed intimately with some substance which will supply oxygen to it and cause it to burn instantaneously. The student can investigate this action by mixing upon a brick a little powdered magnesium with rather more than its own weight of potassium chlorate. The mixture can be ignited by thrusting a piece of paper into it and setting fire to it. When the flame reaches the powder there is a blinding flash and a cloud of white smoke. The magnesium has been converted into its oxide by the oxygen of the potassium chlorate.

243. **Magnesium oxide**, MgO, is the product of the burning of the metal in air or oxygen. It has been obtained in cubical crystals, but is usually a white powder, not visibly crystalline. It can not be completely melted in the oxyhydrogen flame, but melts and boils at the temperature of the electric arc.

It is remarkable as being the only oxide which undergoes no change when heated to the temperature of the arc in contact with carbon. With all other oxides the oxygen combines with the carbon to carbon monoxide, CO, and the metal is liberated, or else combines with more carbon, producing a *carbide*. Thus, when zinc oxide is treated in this way the products are carbon monoxide and zinc vapor, while on the other hand, when lime is mixed with carbon and heated to this temperature, carbon monoxide and calcium carbide, CaC_2, are produced. But magnesium oxide is not affected, except that it will melt and vaporize if the heating is prolonged.

Magnesium oxide is scarcely soluble in water, but dissolves readily in acids, forming magnesium salts. Under the name " calcined magnesia " it is employed in medicine.

244. *Magnesium sulphate*, $MgSO_4$, like many other metallic salts, can form crystals with different amounts of water, depending upon the temperature at which its solution in water is made to crystallize. The following substances are known in this case:

$$MgSO_4,H_2O.$$
$$MgSO_4,6H_2O.$$
$$MgSO_4,7H_2O.$$
$$MgSO_4,12H_2O.$$
$$MgSO_4,24H_2O.$$
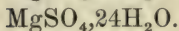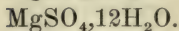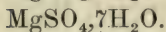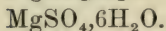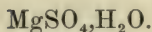
Taken together, these are called the *hydrates* of magnesium sulphate. The forms of the crystals of different hydrates of the same salt are different, and the rule holds good that the lower the temperature at which the solution is made to crystallize the more water in the hydrate produced. Thus, in this case, the hydrates with $12H_2O$ and $24H_2O$ can only exist below $0°$; above that temperature they decompose, even under water, thus:

$$MgSO_4.12H_2O = MgSO_4.7H_2O + 5H_2O.$$
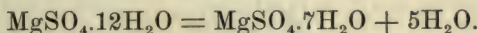
$MgSO_4.7H_2O$ is obtained when the liquid is allowed to crystallize at ordinary temperatures. When it is heated slightly above the boiling-point of water it decomposes, yielding $MgSO_4.H_2O$—

$$MgSO_4.7H_2O = MgSO_4.H_2O + 6H_2O.$$
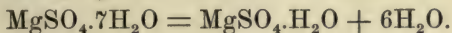
And this, when heated still higher, loses the last molecular weight of water, leaving the anhydrous sulphate $MgSO_4$.

It is likely that all salts containing water of crystallization behave in a similar way. We shall only have time to study the most important hydrate in each case, which is usually that one formed when the solution crystallizes at room temperature, but the student should be careful not to get the false idea that this is the only hydrate that can exist.

Epsom salts, $MgSO_4.7H_2O$, is white and freely soluble in water. The solution has a bitter taste and purgative action. It is used in medicine for this reason, and also as an antidote for lead poisoning. It converts the soluble

lead compounds in the body into lead sulphate, which is insoluble and harmless.

245. *Magnesium chloride,* $MgCl_2$, is contained in seawater, and in large quantities in the water of certain lakes —the Dead Sea, for instance. In such water marine life is impossible. When magnesium chloride is heated with steam it reacts with it, thus:

$$MgCl_2 + H_2O = MgO + 2HCl.$$
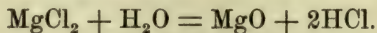
For this reason care must be taken not to use water containing magnesium chloride for steam boilers. The hydrochloric acid liberated in the boiler rapidly corrodes it.

Magnesium chloride is very soluble in water, and when the solution is evaporated to small bulk, $MgCl_2.6H_2O$ separates in deliquescent crystals.

CHAPTER XXIV

THE ZINC GROUP (Continued)

ZINC AND CADMIUM.

ZINC, $Zn = 65.5$.

246. Occurrence and preparation.—Metallic zinc occurs in nature, but is rare. Two important ores are the carbonate, $ZnCO_3$, and the sulphide, ZnS, which is called zincblende. Traces of zinc compounds are found in the human liver, in eggs, and in the ashes of plants which grow from soils in which zinc is present.

Either zinc carbonate or zinc sulphide can be converted into zinc oxide by proper heating. With the carbonate the equation is—

$$ZnCO_3 = ZnO + CO_2.$$
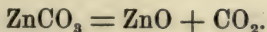
The sulphide must be carefully heated in a current of air, for oxygen takes part in the process:

$$ZnS + 3O = ZnO + SO_2.$$
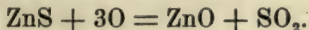
The zinc oxide is then mixed with pounded coal and heated to whiteness:

$$ZnO + C = CO + Zn.$$

The zinc vaporizes and is condensed. Commercial zinc is not pure. It contains traces of iron, lead, arsenic, carbon, and other elements. Pure zinc is best obtained from it by repeatedly distilling it in a vacuum.

247. Properties.—Zinc is a bluish-white lustrous metal, brittle at ordinary temperatures, but malleable when heated

177

to 100°. At 200° it again becomes brittle. It is about seven times as dense as water, and melts below a red heat. When zinc is heated above its melting-point in a covered crucible it takes fire, when the cover is removed, and burns with a blue-white flame, filling the air with white flakes of zinc oxide. We have seen (p. 36) that commercial zinc readily dissolves in dilute hydrochloric or sulphuric acid, and that this is a convenient method of making hydrogen. Pure zinc, on the contrary, is not affected by either acid, but if a little finely divided platinum or copper is present with the zinc, the latter is rapidly attacked.

Zinc is largely employed in the manufacture of brass and for the extraction of silver from lead (p. 152). *Galvanized iron* is simply iron plated with zinc. The surface of the iron is carefully cleansed, and it is then dipped into molten zinc and allowed to cool.

248. **Zinc oxide,** ZnO, can be made by burning the metal in the air. In making it on the large scale, low-grade zinc ores are heated with coal, and the zinc vapor, instead of being condensed, is allowed to burn and collected as zinc oxide. It is a white powder, which becomes sulphur yellow when heated, and returns to its original white when cold. It is insoluble in water, but dissolves readily in acids. Under the name " zinc white," it is largely used as a basis of white paint.

249. **Zinc sulphide,** ZnS.—When powdered zinc is mixed with sulphur and a flame applied, the mixture burns explosively, producing a dense white smoke of zinc sulphide. Zinc sulphide occurs in nature as zinc-blende, which is sometimes colorless and transparent, but usually black or brown, owing to the presence of iron sulphide. It is the most important ore of zinc. When soluble sulphides are added to solutions of zinc salts—that is, when $\overset{=}{S}$ ions and $\overset{++}{Zn}$ ions are

brought together—zinc sulphide is obtained as a pure white precipitate, e. g. :

$$ZnCl_2 + Na_2S = ZnS + 2NaCl.$$
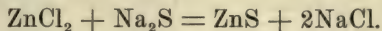
250. **Zinc sulphate,** $ZnSO_4$, can be obtained by dissolving zinc or zinc oxide in sulphuric acid. Several hydrates exist, of which $ZnSO_4.7H_2O$ is best known. It is used in medicine as a violent emetic. Wood soaked in zinc sulphate solution is protected to some extent both from fire and decay.

The compounds of zinc with the *halogens* [1] are all colorless and very soluble in water. Zinc chloride, $ZnCl_2$, which can be obtained by burning the metal in chlorine, or, better, by dissolving it in hydrochloric acid, is the most important. Its solution in water is used as an embalming fluid, and also for cleansing the surface of metals before soldering.

Soluble zinc compounds are *poisonous,* the chloride being the most dangerous. Since water, in presence of air, has a decided action upon zinc, it ought not to be passed through pipes or preserved in vessels lined with the metal. Workmen about zinc furnaces sometimes suffer from a kind of slow poisoning, but this may be partly due to the arsenic which ores of zinc usually contain.

CADMIUM, Cd = 112.

251. Cadmium occurs in nature along with zinc, which it strongly resembles. It is a tough, white metal, not very hard, and slightly denser than zinc.

Many alloys of cadmium have very low melting-points, and it is employed in the production of *fusible metal,* which is an alloy of tin, lead, bismuth, and cadmium, and melts easily below the boiling-point of water. This alloy is used

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[1] The four elements fluorine, chlorine, bromine, and iodine resemble each other greatly. Taken together, they are called the *halogens.*

in the construction of automatic fire-extinguishing appara-
tus. Tubes supplying water are closed with plugs of fusible
metal, so that the heat of the fire melts the plug and re-
leases the water.

Cadmium oxide, CdO, is the product of the burning of
the metal in the air or oxygen. It is a brown, crystalline
powder.

Cadmium sulphide, CdS, occurs in nature, and can be
made by allowing hydrogen sulphide gas to bubble through a
water solution of cadmium chloride:

$$CdCl_2 + H_2S = CdS + 2HCl.$$
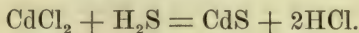
Under the name "*cadmium yellow*" it is much used as a
color in oil paints and for coloring toilet soaps. It is a
bright yellow powder, insoluble in water.

CHAPTER XXV

MERCURY

Hg = 200.

252. Historical.—Mercury was known to the ancients. All through the middle ages, metals which we now know to be elements—copper, lead, silver, and gold, for example— were regarded as compounds of mercury with other constituents, chiefly sulphur and salt. It was supposed to be the mercury in them which gave them their luster. This baseless notion was responsible for the efforts of the alchemists —lasting more than a thousand years and not yet entirely over—to prepare silver and gold from the other metals.

253. Occurrence and preparation.—Mercury occurs native in drops distributed through slates and sandstones, but the chief ore is *cinnabar*, mercuric sulphide, HgS. This occurs in dark-red, lustrous crystals, and is abundant in a few localities—e. g., in Spain, California, and Mexico. For the extraction of the metal, the sulphide is roasted in a current of air. When most sulphides are treated in this way, sulphur dioxide, SO_2, and the oxide of the metal are produced. But mercuric oxide is decomposed by heat, and therefore the metal is formed:

$$HgS + O_2 = SO_2 + Hg.$$
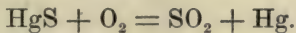
The mercury condenses in stone chambers, through which the gases are led.

254. Properties.—Mercury is one of the two liquid elements, bromine being the other. It has a strong silver-white

metallic luster which is permanent in the air. At —39° it freezes to a lustrous metallic mass which can be beaten out under the hammer like lead. Liquid mercury vaporizes slowly at ordinary temperatures, and if some be placed in the bottom of a bottle and a piece of gold leaf suspended from the cork above it, the gold will slowly turn white from mercury deposited upon it. At 357°, under one atmosphere pressure, mercury boils, passing into a colorless vapor. The density of this vapor, referred to hydrogen, is 100. Therefore the molecular weight must be $100 \times 2 = 200$. Since the atomic weight is also about 200, the molecule of mercury can contain but one atom; the atom and the molecule are identical. The same thing is true of other metals in the state of vapor, and, we have reason to think, in the solid and liquid state also.

Mercury is not affected by water at any temperature, nor by oxygen or air in the cold. Heated just below its boiling-point in the air it slowly passes into a red powder of mercuric oxide, HgO. The metal is easily dissolved by nitric acid, which, when cold and dilute, produces mercurous nitrate, $Hg_2(NO_3)_2$; when hot and stronger, mercuric nitrate, $Hg(NO_3)_2$.

255. From the last sentence it will be seen that there are two sets of salts of mercury. For example:

	Mercurous salts.	Mercuric salts.
Chloride	Hg_2Cl_2	$HgCl_2$
Nitrate	$Hg_2(NO_3)_2$	$Hg(NO_3)_2$
Sulphate.............	Hg_2SO_4	$HgSO_4$

The structure of the mercuric salts is simple, the mercury being bivalent, e. g.:

$$\text{Mercuric chloride, } Hg{<}^{Cl}_{Cl.}$$

In the mercurous compounds we think of the two mercury atoms as linked together, e. g.:

$$\text{Mercurous chloride, } \begin{array}{l} Hg{-}Cl \\ | \\ Hg{-}Cl. \end{array}$$
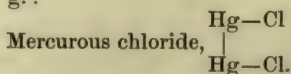
The mercury, then, is still bivalent in the mercurous compounds. In solutions of mercuric compounds the mercury exists as ions $\overset{++}{Hg}$, while in mercurous solutions the ion is $\begin{smallmatrix} \overset{+}{Hg} \\ | \\ \overset{+}{Hg} \end{smallmatrix}$. The chemical behavior of these two ions is very different.

The student should never accept doubled formulas on faith, but should form the habit of inquiring what facts cause us to double them. When we do not know what the molecular weight of a compound is, it is proper to use the simplest formula which will express its chemical composition. This we do, for instance, with substances like silver chloride, AgCl, and mercuric oxide, HgO, whose molecular weights are unknown at present. But when we double the formula we must have facts which support us in so doing if the formula is to have any meaning. In this case the facts are these: the density of the vapor into which pure dry mercurous chloride is converted by heat is about 235.5; therefore, the molecular weight is 235.5 × 2, or 471, and the formula must be Hg_2Cl_2. Further, the molecular weight of mercurous nitrate dissolved in water (p. 124) is found to agree with the formula $Hg_2(NO_3)_2$, not $HgNO_3$.

256. **Mercurous compounds.**—*Mercurous chloride*, Hg_2Cl_2, is largely used in medicine under the name "calomel." It can be made by heating gently an intimate mixture of mercuric chloride and mercury when it vaporizes and is condensed:

$$HgCl_2 + Hg = Hg_2Cl_2.$$
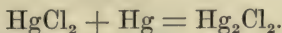
It is white, crystalline, and insoluble in water. When heated, it vaporizes without melting. Like silver chloride, it darkens on exposure to light.

Mercurous nitrate, $Hg_2(NO_3)_2$, is the most important soluble mercurous salt. It is produced when mercury dissolves in cold dilute nitric acid.

257. **Mercuric compounds.**—*Mercuric oxide*, HgO, is obtained by heating mercuric nitrate:

$$Hg(NO_3)_2 = HgO + 2NO_2 + O.$$
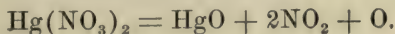
It is a dense, red, crystalline powder, which slowly decomposes in light into mercury and oxygen. The color of mercuric oxide, like that of many other substances, depends upon the temperature. At —200° (the temperature of boiling liquid air) it is sulphur-yellow, at room-temperature red, at higher temperatures black. Below a red heat it separates into mercury and oxygen (p. 26).

Mercuric sulphide, HgS, is the mineral *cinnabar.* A brilliant scarlet variety of it, called *vermilion,* is made by grinding mercury and sulphur together in presence of a solution of potassium sulphide, K_2S. This is much used as a coloring matter. The dense black precipitate which is formed when hydrogen sulphide is passed into a solution of a mercuric salt is mercuric sulphide.

Mercuric sulphide approaches absolute insolubility in water more nearly than any other compound which has been investigated thus far. The cinnabar of nature ranges in color from nearly black to bright red; the shade of vermilion is much affected by the method of preparation, and the precipitated HgS is invariably black. These differences in color are remarkable, and not yet satisfactorily explained.

Mercuric chloride, $HgCl_2$, is produced when the metal burns in chlorine. It can be made by grinding mercuric sulphate with salt and then heating the mixture in large glass flasks. The vapor of mercuric chloride condenses to a white compact mass in the upper cool portion of the flask, which is broken in order to remove it:

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$
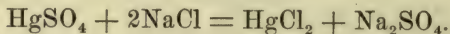
Mercuric chloride is a dense, white, crystalline salt, which melts first, and then vaporizes, when heated. It is freely soluble in water, and the solution is almost a non-conductor of the current, showing that, unlike most other salts, mercuric chloride scarcely separates into its ions when dissolved. It is intensely poisonous, and the antidote is some

form of albumin—for instance, raw eggs taken at once—
for albumin forms with it an insoluble compound. Mer-
curic chloride is one of the best of all antiseptics and dis-
infectants, and the dilute water solution is largely used for
this purpose in surgery.

Mercuric iodide, HgI_2, separates when a potassium iodide
solution is added to one of mercuric chloride as a precipitate
which is at first yellow, but turns red at once. An excess
of either potassium iodide or mercuric chloride will redis-
solve it. Mercuric iodide is an intensely red crystalline pow-
der. We have already discussed its behavior when heated
(p. 24). It is insoluble in water, but soluble in alcohol and
in water containing potassium iodide.

258. **The amalgams.**—This name is given to the alloys
which mercury forms with other metals. They are very in-
teresting because they are probably similar in character to
other alloys, and, owing to the fact that mercury is a liquid,
they are much easier to make and to work with. Hence we
may expect their study to throw light upon the nature of
alloys in general—an interesting question. The amalgams
are silver-white, crystalline, metallic solids. They are some-
times said to be pasty masses, but this is because too much
mercury was used in making them and the soft product was
a mixture of the real amalgam with liquid mercury.

Mercury usually forms several amalgams with the same element.
Thus, with sodium, the compounds $NaHg_5$ and $NaHg_6$ are known,
and with potassium, the compounds KHg_{10}, KHg_{12}, and KHg_{14}.
KHg_{14} can only exist below 0°, at which temperature it separates
into KHg_{12} and mercury—

$$KHg_{14} = KHg_{12} + 2Hg.$$
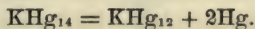
From 0° to 73° KHg_{12} exists. At the latter temperature it sepa-
rates, thus:

$$KHg_{12} = KHg_{10} + 2Hg.$$
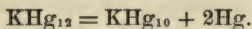
So with other amalgams. Those richer in mercury can only exist at
low temperatures, and when heated, split up, yielding mercury and
amalgams poorer in it. It will be seen that the mercury in the

amalgams behaves very much in the same way as the water in salts containing water of crystallization (p. 175).

259. General remarks on the calcium and zinc groups.— The relation between the calcium group and the zinc group is similar to that between the sodium group and the copper group. Like the sodium group, the calcium group is composed of strong metals—using the word in its chemical sense —which are energetically acted upon by water, forming their hydroxides, and these hydroxides are strong bases. Their susceptibility to the action of water prevents calcium, strontium, and barium from receiving any application as metals.

On the other hand, the metals of the zinc group are either slightly or not at all affected by water and air, and are accordingly employed in the metallic state for various purposes. Mercury, like gold, is not affected by the atmosphere at all, and will retain its luster unchanged for any length of time.

What is the chemical difference between the " noble " metals, like silver, gold, and platinum, and the so-called " base " metals, like lead, iron, and zinc ? The difference is simply one of chemical activity. Gold is an inert element. Its tendency to enter into chemical combination with other elements is small, and hence its luster is unaffected by the atmosphere even at high temperatures. Iron, on the contrary, possesses a much stronger tendency to take part in chemical reactions. Therefore, at the surface of a piece of the metal there begins a chemical change in which the water and oxygen of the air convert the surface of the iron into a reddish-brown hydroxide called " rust." And, in general, the chief distinction between the " noble " metals and the common metals is that the latter are far more active chemically. We must remember also that the noble metals are not very abundant in nature, and are accordingly high in price. The metals of both the calcium and the zinc groups are almost always bivalent.

CHAPTER XXVI

BORON AND ALUMINIUM

Boron, B.   Aluminium, Al.

260. Boron is unmistakably a non-metal. It has none of the physical properties of a metal, it forms a gaseous hydrogen compound (BH_3), yields no salts with acids, and its hydroxide is an acid. Aluminium is physically a metal, and for the most part chemically also, though its hydroxide is only a feeble base. Both elements are almost always trivalent.

Boron, B = 11.

261. **Occurrence.**—Boron occurs in nature as boric acid or salts of boric acid. Boric acid itself, $B(OH)_3$ (boron hydroxide), is contained in the steam which issues from the ground in volcanic regions, particularly in Tuscany. Around such a steam-jet a stone basin is built in such a way that the steam is made to bubble through water in the basin. The boron hydroxide dissolves in this water, which, after being treated with steam in several such basins, is evaporated to recover it. For this purpose the heat of the volcanic steam is employed, so as to save the expense of artificial fuel. The liquid is made to flow slowly over a long inclined lead plate, which is heated by steam passing beneath it. *Borax*, $Na_2B_4O_7.10H_2O$, is largely obtained from the water of certain lakes in California, Ceylon, and elsewhere.

262. Preparation and properties.—Boron can be obtained by heating boron oxide B_2O_3, with sodium or magnesium:

$$B_2O_3 + 6Na = 3Na_2O + 2B,$$
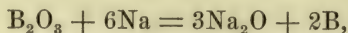
or by heating potassium in boron fluoride, which is a gas:

$$BF_3 + 3K = B + 3KF.$$
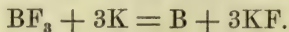
It is a brown powder, odorless and tasteless, and slightly soluble in water. Heated in the air or in oxygen, it burns brightly to B_2O_3. At a high temperature it combines with nitrogen when heated in the gas, producing boron nitride, BN, a white powder.

Boron oxide, B_2O_3, is made by strongly heating the hydroxide—

$$2B(OH)_3 = B_2O_3 + 3H_2O.$$
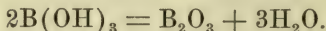
It is a colorless, brittle, glassy mass, which melts readily, but only vaporizes at very high temperatures.

The preparation of *boron hydroxide*, $B(OH)_3$, has just been described. It forms colorless crystals which are soluble in water and in alcohol. The latter solution burns with a beautiful green flame, and this peculiarity is used as a test for boron hydroxide. Boron hydroxide is feebly acid to litmus, and reacts with bases forming salts in which its hydrogen is replaced by various metals. It is therefore called *boric acid,* and its salts are called the *borates.* The dilute water solution of boric acid forms an excellent wash for sore or inflamed eyes. Large quantities of the acid are used for the manufacture of borax.

263. Borax, $Na_2B_4O_7.10H_2O$, forms colorless crystals, which give off flashes of light when crushed in the dark. It is freely soluble in water, and the solution has a peculiar cooling taste.

When borax is strongly heated the water of crystallization escapes and the liquid which is left solidifies on cooling to a hard, brittle, glassy mass called borax glass, which

FRIEDRICH WÖHLER
B. Germany, 1800. D. 1882.

is simply $Na_2B_4O_7$. Borax glass dissolves many compounds of the metals, and is often colored by them in such a way that the metal can be identified. This behavior is used in analysis. Thus, if we heat a little borax on a platinum wire, it swells up, and finally, when the steam has all escaped, solidifies on cooling to a colorless bead of borax glass. If, now, we cause a fragment of cobalt nitrate (or any other cobalt compound) to adhere to the bead, and heat it again, it becomes deep sapphire blue. If, instead of a cobalt salt, we use a compound of manganese, the bead is colored amethyst.

When carbon and boron are heated together to a very high temperature, they combine, producing CB_6, a black crystalline compound, which is interesting on account of its extreme hardness. It is about as hard as the diamond, and its powder can be used, instead of diamond dust, for cutting the gem.

ALUMINIUM, Al = 27.

264. Occurrence.—Aluminium does not occur native, but its compounds are plentiful. In abundance it is third among the elements, making up nearly 8 per cent of the earth's crust. Particularly common are compounds of aluminium with *silicon* and oxygen, called silicates of aluminium. Clay is a compound of this class, having, in pure condition, the composition $Al_2Si_2O_7$ with water. The various felspars—most important rock-forming minerals—are also aluminium silicates, but they contain other metals, particularly sodium, potassium, and calcium. Cryolite, which occurs abundantly in Greenland, is a fluoride of aluminium and sodium, $AlF_3 3NaF$. It is employed in the manufacture of aluminium, and also, on account of its sodium, in the production of sodium carbonate.

265. Preparation.—Aluminium was first obtained by heating the chloride with potassium, and for a long time a

similar method was used in preparing it. It is now made on the large scale by an electrolytic process which has greatly reduced its price.

The mineral cryolite melts at a low temperature and the liquid dissolves aluminium oxide, Al_2O_3. When the current from a dynamo is passed through the solution, only the Al_2O_3 is decomposed, the cryolite not being affected. In practice cryolite is melted in a vessel lined with carbon, and aluminium oxide added. Then a bundle of carbon
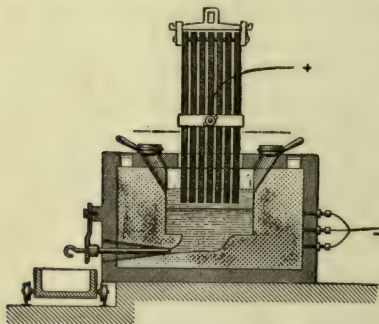

Fig. 35.—Industrial production of aluminium by electrolysis.

rods is connected with the positive pole of the current from a dynamo and dipped into the liquid. The vessel itself is connected with the negative pole. When the current passes, the aluminium, like all metals, goes to the negative pole and collects, in the melted state, below the melted cryolite. From time to time it is withdrawn and fresh aluminium oxide added, so that the process is continuous (Fig. 35).

266. **Properties.**—Powdered aluminium is gray; the compact metal has about the color and luster of tin. It is very light, the density being about that of glass—2.7—and very malleable and ductile. Since its tenacity is only about $\frac{1}{5}$ that of steel, it has no chance of displacing the latter for structural purposes.

Aluminium melts at a clear red heat to a thin liquid, and vaporizes only at the very highest temperatures. It is not acted upon by either dry or moist air, and in compact masses not much affected by being heated in air or oxygen. As powder it burns brightly when heated. Aluminium is

not acted upon by nitric acid nor by dilute sulphuric acid. It dissolves readily in hydrochloric acid and in solutions of the hydroxides of potassium or sodium, hydrogen escaping in both reactions. The metal, especially in the presence of salt, is somewhat readily attacked by the acids which are present in fruits and vegetables, and has not proved very successful as a material for cooking utensils.

267. **Uses.**—*Flash-light powders* containing aluminium have recently appeared, and if they are successful the metal will entirely displace magnesium for this purpose, for it is much cheaper. When a little aluminium is added to melted steel just before it is poured into the mold, the casting obtained is solid and free from " blow-holes "—little cavities which have a very bad effect on the strength of the steel. The metal is largely used for this purpose.

At a high temperature, aluminium acts upon metallic oxides, combining with the oxygen and liberating the metal, e. g.:

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr.$$
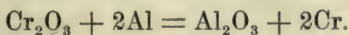
Much energy is evolved in the change, and an extremely high temperature (3000°) produced. Manganese and chromium are now made commercially by this method.

Many *alloys* containing aluminium have been made. The most important is *aluminium bronze,* which contains 5 to 8 per cent of aluminium, the rest being copper. It has about the color of gold, is very rigid and strong, and is unaffected by air and water. Its properties make it valuable for many purposes.

268. **Aluminium oxide,** Al_2O_3, is the mineral *corundum.* When perfectly transparent and free from flaws it forms, when tinted red by the presence of a little chromium, the ruby; when blue by traces of cobalt, the sapphire. Both of these gems have been made artificially. An impure form of corundum, dark from the presence of iron oxide, is called

emery. Aluminium oxide can be made artificially by burning the metal in the air or by heating the hydroxide. Crystallized aluminium oxide is intensely hard. Among minerals, it stands next to the diamond in this respect, but some artificial products are known which must be placed between the two.

269. *Aluminium hydroxide,* $Al(OH)_3$ is precipitated in gray flakes when aluminium ions, $\overset{+++}{Al}$, and hydroxyl ions come together—i. e., when a solution of a base, like $NaOH$, is added to a solution of an aluminium salt, like $AlCl_3$. It is soluble in acids producing aluminium salts, and soluble also in solutions of bases producing compounds called *aluminates* in which its own hydrogen is replaced by metals, e. g.:

$$Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O.$$
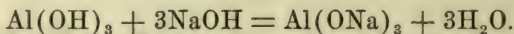
$Al(ONa)_3$ is sodium aluminate. Thus, $Al(OH)_3$ acts like a base with acids and like an acid with bases. Heat converts aluminium hydroxide into the oxide:

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$
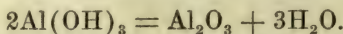
270. **Aluminium sulphate,** $Al_2(SO_4)_3$, can be made by boiling clay with sulphuric acid. It forms pearly scales containing $18H_2O$, which are freely soluble in water. It is largely used in dyeing, not as a color, for it is colorless, but for the purpose of causing dyestuffs to adhere to the fabric. Cotton, in the presence of aluminium sulphate, is permanently colored by many dyes which do not affect it when alone. A substance which behaves in this way is called a *mordant* by the dyer. Formerly mordants were universally employed in dyeing cotton fabrics, but now numerous dyes are known which color cotton perfectly without their aid.
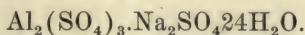
Ordinary ALUM is a double sulphate of potassium and aluminium:

$$Al_2(SO_4)_3 \ \ K_2SO_4.$$
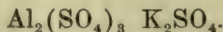
When it has been crystallized from water it contains, in addition, $24H_2O$, so that the composition of alum in crystals is

$$Al_2(SO_4)_3.K_2SO_4.24H_2O.$$
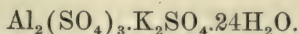
This is potassium alum. Many univalent metals form similar alums. Thus sodium alum is

$$Al_2(SO_4)_3.Na_2SO_4 24H_2O.$$

Ammonium, NH_4, which acts so much like sodium in other respects, also forms an alum:

$$Al_2(SO_4)_3(NH_4)_2SO_4 24H_2O.$$
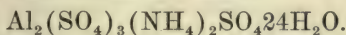
This is *ammonium alum*, and is an important alum of commerce.

Further, we may have other trivalent metals in place of aluminium in an alum. Thus, chromium alum, known in trade as " chrome alum," is

$$Cr_2(SO_4)_3K_2SO_4.24H_2O,$$
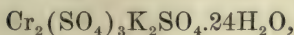
and, just as with the aluminium alums, so here, other univalent metals can take the place of the potassium. The total number of different alums is therefore very great. They are very similar to each other, all crystallizing in the same form (Fig. 36).


FIG. 36.—Alum crystals.

271. Two or more substances which crystallize in the same form are said to be *isomorphous*, and isomorphism is frequently connected, as it is here among the alums, with a close similarity in chemical make-up. This fact is a valuable help at times in determining the atomic weight of an element. Thus, suppose the atomic weight of rubidium to be unknown. We make the rubidium alum, whose formula, if it is similar to the potassium alum, must be

$$Al_2(SO_4)_3Rb_2SO_4 24H_2O.$$
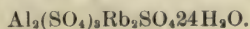
Now the amount of potassium in a molecular weight of the potassium alum is $39 \times 2 = 78$ parts; and when we analyze the rubidium alum we find that it requires 170 parts of rubidium to play the same *rôle*. But since the two compounds are isomorphous, their formulas are in all probability similar, and these 170 parts are probably two atomic weights, Rb_2. Hence the atomic weight of rubidium is probably $\frac{170}{2} = 85$.

The alums can be made by bringing solutions of the two single sulphates together when they crystallize out, being less soluble in water than the salts singly. Thus, when strong potassium sulphate and strong aluminium sulphate solutions are mixed, potassium alum separates in crystals.

272. *Aluminium chloride*, $AlCl_3$, is best made by heating cuttings of the metal to redness in a wide glass tube, while a rapid current of hydrochloric acid gas is passed over them. It forms colorless crystals, which rapidly dissolve in water, the liquid becoming warm. The water solution is acid to litmus and other indicators, and therefore must contain hydrogen ions. As a matter of fact, when aluminium chloride is dissolved in water, a reaction occurs which liberates hydrochloric acid:

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl.$$
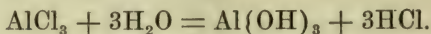
Since the hydrochloric acid is dissociated into $\overset{+}{H}$ and $\overset{-}{Cl}$ ions, the liquid is acid. Whenever the solution of a salt is found to be acid, a reaction of this sort must have occurred between the salt and the water (p. 127).

CHAPTER XXVII

THE CARBON GROUP

Carbon, C.   Silicon, Si.   Tin, Sn.   Lead, Pb.

273. The elements of this group are usually quadrivalent, though tin and lead form many compounds in which they are bivalent.

Carbon and silicon are non-metals; tin and lead are metals.

Carbon is such an important element that we shall leave it to the last, and study it somewhat more in detail than the others.

SILICON, Si = 28.5.

274. **Occurrence.**—Silicon, although it never occurs free in nature, stands next to oxygen in abundance, making up more than one-fourth of the rock-masses of the earth's crust. Its oxide, SiO_2—called quartz—is the most common of minerals. Compounds of the metals with silicon and oxygen, called silicates, make up the great bulk of most important rocks, like granite, gneiss, and serpentine. Asbestos is a silicate of magnesium, $MgSiO_3$, usually containing calcium also. In fact, limestone (p. 169) is the only rock of importance which is not made up of silicon compounds.

275. **Properties.**—Silicon is a brown, lusterless powder which melts and volatilizes only at the very highest temperatures. It is unaffected by water and by acids, except hydrofluoric acid, HF, which produces silicon fluoride and

hydrogen. When heated in air or oxygen, it burns brightly to the oxide.

There is another modification of the element. This forms black shining crystals, which do not burn when heated in the air or in oxygen, and are not acted upon by hydrofluoric acid.

**276. Hydrogen silicide, SiH₄.**—Some finely powdered quartz is mixed with about $1\frac{1}{2}$ times its weight of powdered magnesium and the mixture carefully heated in a dry test-tube. It is sufficient to heat one point of the mass; this starts the reaction, and the whole contents of the tube become incandescent. When the tube cools, we find in it a black, friable mass, which is mainly magnesium silicide, $SiMg_2$. The following reaction has occurred:

FIG. 37.—Hydrogen silicide.

$$SiO_2 + 4Mg = SiMg_2 + 2MgO.$$
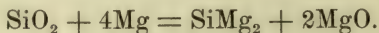
When some of the powdered substance is thrown into dilute hydrochloric acid in a beaker, bubbles of a colorless gas rise through the acid and take fire spontaneously as soon as they reach the surface, burning with a slight explosion and giving off puffs of white smoke. This gas is *hydrogen silicide*, SiH_4, produced thus:

$$SiMg_2 + 4HCl = SiH_4 + 2MgCl_2.$$
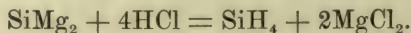
In preparing larger quantities of the gas, the apparatus shown in Fig. 37 is used. The magnesium silicide is first introduced into the gas-generating bottle, which is small. Then water is poured in through the funnel-tube until all air has been expelled. This is necessary, for if any air were left, the first SiH_4 evolved would ignite spontaneously and produce an explosion.

The next step is to pour strong hydrochloric acid gently through the funnel-tube. A colorless gas escapes in bubbles through the water in the dish. Each bubble burns spontaneously, producing a bright flash of light and a white ring of smoke. This smoke is silicon oxide, SiO_2; the burning of the gas is described by this equation:

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O.$$
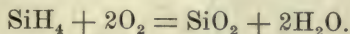
There is nothing mysterious about this spontaneous inflammation. Iron burns only at very high temperatures; charcoal at a red heat; illuminating gas catches fire from a flame but not from a match-stick bearing a spark; the vapor of carbon disulphide is inflamed by a glass rod heated slightly above 100°; finally, the temperature of ignition of the gas we have just made is below the ordinary temperature of the air. No doubt it would be possible to cool our gas and air separately to such a temperature that no combustion would occur when they were brought together, though this experiment has never been tried.

Pure hydrogen silicide does *not* take fire spontaneously, though it is very inflammable. Our gas contains a little hydrogen, and this mixture possesses a lower temperature of ignition than the pure gas.

277. Silicon oxide, SiO_2—also called *silica*—results when silicon is burned in the air or when silicon hydroxide is heated. Obtained in this way, it is a loose white powder, insoluble in water and in acids except hydrofluoric acid, which converts it into silicon fluoride and water:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$
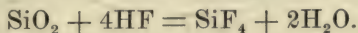
Silicon oxide melts to a thin liquid in the oxyhydrogen flame and vaporizes at the temperature of the electric arc. It occurs in nature in great abundance, as the mineral *quartz,* which forms crystals like those shown in Fig. 38. Pure quartz is perfectly colorless and transparent, and owing to this it was supposed, until very recent times (end

of the sixteenth century), to be water which had been subjected to intense cold and so completely frozen that it was
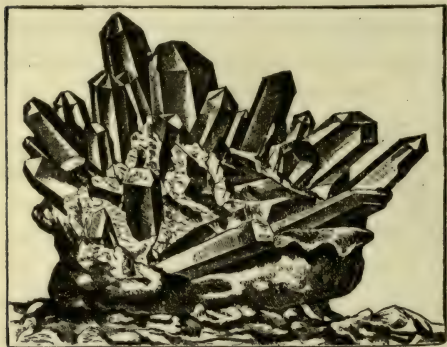

FIG. 38.—A mass of quartz crystals.

impossible to melt it. Quartz is often colored by traces of impurities, probably compounds of carbon and hydrogen with other elements. Colored violet, it forms the amethyst, while transparent, yellow quartz is a cheap variety of topaz.

Quartz is quite hard, and is very inert chemically. It is unaffected by the agencies which dissolve most other minerals or cause them to crumble and form soil. Thus, when a rock containing it is destroyed, the quartz remains. In this way it comes about that the sand of sea- and river-beaches consists very largely of quartz. When such sand becomes cemented to a rock, the result is what is called a *sandstone*. Owing to the hardness of quartz, fine-grained sandstones make excellent whetstones.

Silica also occurs in nature uncrystallized. This is called *opal*. Its composition is the same as that of quartz, but it is more impure, frequently containing small quantities of iron and aluminium oxides and, almost invariably, water. When it is compact, translucent, and exhibits a beautiful play of colors, it forms the gem *opal*.

278. ~~Silicon hydroxide~~ (*silicic acid*).—When we studied nitrous acid we made the acquaintance of an acid which is known only in its salts, and when liberated from them at once decomposes (p. 117). Silicic acid behaves in the same way. Silicon being quadrivalent, the composition of its

~~hydroxide~~ acid—which is called silicic acid—would be $Si(OH)_4$. $+, SiO_4$
Salts in which its hydrogen is replaced by metals are among
the most important minerals. They are called *silicates*.
Thus, magnesium silicate, Mg_2SiO_4, is called *olivine*, and a
silicate in which half of the hydrogen is replaced by copper
is called *dioptase*, CuH_2SiO_4. Hundreds of silicates occur
in nature, and many of them are much more complex in
composition than these, but they are all compounds of
metals with silicon and oxygen.

279. **Glass** has a similar chemical make-up. When silica
is fused with calcium carbonate and sodium carbonate, cal-
cium silicate and sodium silicate are formed, both liquid
at the temperature of the glass furnace. These two liquids
mix in all proportions (like water and alcohol), and when
the substance cools it solidifies without any separation,
forming a solid solution of sodium and calcium silicate.
If the glass is cooled too slowly so that there is time for
crystallization to take place, the solid solution is trans-
formed into a mass of small crystals of sodium silicate and
of calcium silicate; it becomes white and opaque, and the
glass is spoiled. This interesting change is called *devitrifi-
cation,* and it takes place even in solid cold glass, though
very much more slowly, so that very old glass frequently be-
comes dull white and semi-opaque.

Ordinary window and bottle glass contains mostly so-
dium and calcium silicates, and the green color which it
often has is due to the presence of a little iron silicate.
When lead oxide is added to the materials in the melting-
pot, the resulting glass will also contain lead silicate. This
gives it a greater density and a higher refractive index.
Such glass is used for lenses and prisms.

When potassium carbonate, instead of sodium carbo-
nate, is melted with quartz and calcium carbonate, the glass
will contain potassium and calcium silicates. Such glass is
called *Bohemian glass.* More sand is used in making it,

and it therefore contains a higher percentage of SiO_2 than ordinary glass. It melts at a higher temperature and is less attacked by most liquids. For this reason it is largely used in making chemical glassware.

It will be seen that glass varies greatly in composition. This agrees with the statement that it is a solid solution, not a chemical compound. In the latter case such variation would be impossible (p. 33).

280. *Sodium silicate* is soluble in water, and is called *water-glass*. We should expect, by adding an acid to this solution, to obtain silicic acid, thus:

$$Na_4SiO_4 + 4HCl = 4NaCl + Si(OH)_4.$$
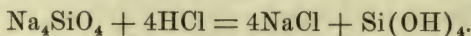
When the experiment is tried, a colorless jelly separates which, when it dries, becomes a white solid. However, analysis shows that neither the jelly nor the solid is silicic acid, but simply a mixture of SiO_2 with variable quantities of water.

$CaCO_3 + SiO_2 = CaSiO_3$

$Na_2CO_3 + SiO_2 = Na_2SiO_3$

glass (window (soda

K instead of Na Bohemian g Cas

CHAPTER XXVIII

THE CARBON GROUP (Continued)

Tin, Sn = 119.

281. Occurrence.—Bronze, the alloy of tin and copper, was known in prehistoric times, and tin itself was known to the ancients, who considered it to be a light-colored and peculiar variety of lead. It occurs native in small quantities, but the most important ore is tin dioxide, SnO_2, called tin-stone by the miners. This occurs abundantly in southwestern England in the county of Cornwall, in Australia, and especially in the Malay peninsula and the neighboring islands.

282. Extraction.—The first step is to free the mineral from impurities as far as possible. Sulphur and arsenic can be removed by roasting, when they burn away as oxides. Some other impurities can only be separated by a process of hand-picking. Then the purified tin-stone is heated with charcoal or coal in suitable furnaces. The tin obtained in this way is purified by making use of the fact that its melting-point (228°) is far lower than that of the impurities it contains. Thus, when it is fused at a low temperature, almost pure tin runs off and a mass containing the iron, copper, and other metals in the state of tin alloys remains. This is worked up again to remove the tin it contains.

283. Properties.—Ordinary tin is a metal with a brilliant white luster. It is a little harder than lead and about

seven times as dense as water. At 100° it is ductile and malleable; at 200° it is brittle and can be powdered. It melts at a low temperature and boils at a white heat, catching fire if in contact with air, and burning with a bright white flame to tin dioxide. This same transformation takes place more slowly at a lower temperature, when the metal is melted in contact with air. But at ordinary temperatures it is unaffected by air or water.

284. Gray tin.—There is a second modification of tin, a gray, crystalline powder much less dense than ordinary tin. This is produced when tin is subjected to great cold for a long time—for instance, when bars of tin are stored in unheated warehouses during cold winters. Sometimes the tin of organ-pipes in unheated churches is completely converted into the gray variety. The change is very slow, but may be made much more rapid by placing some gray tin in contact with the white tin and putting the whole under some tin chloride solution in a flask. When this is done it is found that below 20° the white tin turns to the gray modification, while above 20° the change takes the reverse direction. The change of the gray variety to the white is rapid. If some gray tin be placed in a beaker and boiling water poured over it, it at once becomes denser, acquires a white metallic luster, and changes completely to the white modification. This change is due solely to the rise in temperature, and the same thing happens if the gray tin is heated in some other way.

285. Uses of tin.—Tin is used in the manufacture of solder, an alloy of tin and lead. Tin-plate is sheet-iron coated with tin by cleaning the surface carefully and dipping it into melted tin. It is employed in making cans for the preservation of fruits. The acids of fruit dissolve a little tin from such vessels, but since tin compounds in small quantities are not poisonous, and there is no cumulative action (pp. 146–207), this is no great matter. Some

of the bar tin of commerce, especially that from the East, is very pure, but the so-called tin-foil, which is used for wrapping food-products, is usually highly impure, and sometimes is nearly pure lead, containing no tin whatever.

Tin forms two series of compounds: the *stannous* compounds, of which SnO and $SnCl_2$ are examples, the tin being bivalent, and the *stannic* compounds—for instance, SnO_2 and $SnCl_4$—in which the tin is quadrivalent.

286. Stannous chloride, $SnCl_2$, is the most important *stannous* compound. It is made by dissolving the metal in hot, strong hydrochloric acid. When the solution is evaporated it separates in white crystals of the composition $SnCl_2.2H_2O$, which are called tin-salt by the dyer, and much used as a mordant.

The stannous compounds tend to pass into stannic compounds. Thus, when solutions of stannous chloride and mercuric chloride are mixed, then, if the stannous chloride is in excess, a grayish-black precipitate of finely divided mercury is produced, stannic chloride being formed:

$$HgCl_2 + SnCl_2 = SnCl_4 + Hg.$$
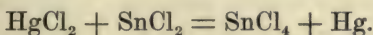
Stannic Compounds

287. Stannic oxide, SnO_2, is found in nature as "tin-stone," called in mineralogy *cassiterite*. Pure tin-stone is colorless, but, as usually found, it varies from yellow to black. Its high density (7) at once distinguishes it from most other minerals. Stannic oxide may be made artificially by burning tin in the air. It then forms a soft white powder, which melts with difficulty and is scarcely affected by acids.

288. *Stannic hydroxide*, $Sn(OH)_4$, is an interesting substance. There are two ways of making it: first, by precipitating a solution of stannic chloride, $SnCl_4$, with a base:

$$SnCl_4 + 4KOH = Sn(OH)_4 + 4KCl;$$
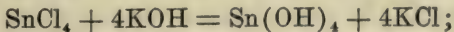
second, by the action of strong nitric acid on tin. The two products are white amorphous powders alike in appearance, and have exactly the same composition, but they are utterly unlike in their chemical conduct. Thus the hydroxide made by the first method is easily soluble in the three ordinary acids, but that prepared by the second is not, and this difference still remains when the two products have been dissolved separately in a liquid which dissolves them both, and then obtained again in the solid state.

The student should compare this curious case with the two modifications of mercuric iodide (p. 24). The state of things is entirely different. The red and the yellow mercuric iodide melt to the same liquid, yield the same vapor, and when they are dissolved separately in the same solvent (e. g., alcohol) the two solutions produced are in all respects identical. In the language of the atomic theory, we may say that the two are different only in the way in which the molecules are arranged in the crystals. Of course, when the substance is liquefied, vaporized, or dissolved, the crystals vanish, and there is no longer any arrangement. But when two substances remain unlike after such treatment, the cause of the difference lies deeper, and can only be explained by the statement that the *atoms in the molecule* are differently arranged in the two cases.

Substances like the two stannic hydroxides, which are alike in composition but different in properties, are called *isomeric.*

Stannic hydroxide in both its forms is an acid, and readily reacts with bases forming salts in which its hydrogen is replaced by metals. It is often called *stannic acid* for this reason, and the salts are called *stannates.*

289. *Stannic sulphide,* SnS_2, crystallizes in scales, which have the color and something of the luster of gold. It is called *mosaic gold,* and has long been used for giving a lustrous metallic surface to plaster casts.

Stannic chloride, $SnCl_4$, is made by melting tin in a retort and passing a current of dry chlorine over it. The vapor is led through a condenser, and stannic chloride collects in the receiver as a colorless, fuming liquid.

Tin amalgam is somewhat employed for the metallic reflecting surface with which the glass of mirrors is backed, but is being replaced by silver for this purpose, owing to the poisonous action of the mercury upon the workmen.

CHAPTER XXIX

LEAD

Pb = 207.

290. Occurrence and extraction.—Lead was known to the ancients. The metal itself is rare in nature. The carbonate $PbCO_3$ and the sulphate $PbSO_4$ occur as minerals, but the most important ore is *galenite,* which is lead sulphide, PbS.

In order to obtain the lead from galenite, it is roasted in a current of air, the sulphur burning away as sulphur dioxide, while the lead remains as oxide. The lead oxide is then heated with some form of carbon (charcoal or coal), when carbon dioxide and lead are produced.

Another method, called the " air-reduction process," is sometimes used with very pure ores. The lead sulphide is roasted until a portion of it is converted into lead oxide; then the access of air is stopped and the temperature raised until the mixture melts. The sulphur of the lead sulphide and the oxygen of the lead oxide escape together as sulphur dioxide, while lead remains:

$$2PbO + PbS = SO_2 + 3Pb.$$
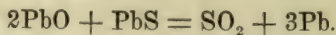
The chief lead-producing countries are the United States, Spain, and Germany.

291. Properties.—Lead is softer than gold. The freshly cut surface has a bright bluish-gray metallic luster, but this rapidly disappears by oxidation, giving place to the familiar dull gray color of the metal. This attack, however, is superficial, and the metal is quite permanent in air,

whether moist or dry. Lead is tolerably malleable, and is plastic at a gentle heat, so that it can be made into tubes, but it is not tenacious and can not be drawn into fine wire.

Lead melts readily and boils at a white heat. Liquid lead absorbs oxygen from the air, passing into lead oxide, PbO.

Pure water has a decided action on lead, converting it into the hydroxide, some of which dissolves; and if some fresh shavings of the metal are covered with distilled water in a beaker and allowed to stand, lead can be detected in the liquid after half an hour. This fact is of interest because lead pipes are used for conveying water, and cases of poisoning have been brought about in this way. However, the water of nature, on account of the salts dissolved in it, acts upon lead much less rapidly than distilled water does, so that if it simply runs through the pipes and is not allowed to stand in them, there is little danger.

Lead is little acted upon by hydrochloric or sulphuric acid, but is readily dissolved by nitric acid.

Compounds of lead are *poisonous*. It requires a large quantity of a lead compound to produce serious symptoms if it is all introduced into the system at once, and this form of lead-poisoning rarely occurs; but *chronic* lead-poisoning —that is, poisoning from the continual absorption of small quantities of lead compounds during months—is frequent and dangerous. All workmen who deal with lead and its compounds are liable to it, though the danger can be reduced by perfect cleanliness. Some of the symptoms are violent pains in the abdominal region, a loss of power over certain muscles (particularly those which move the hand at the wrist), and a slate-colored line round the edges of the gums.

292. Compounds of lead with oxygen.—The most important oxides of lead are *lead oxide,* PbO, *lead dioxide,* PbO_2, and *red lead* or *minium,* Pb_3O_4.

Lead oxide, PbO, is made by heating lead above its melt-

ing-point in the air. It occurs in commerce as a heavy yellow powder, called *massicot,* or as reddish-yellow crystalline scales, called *litharge.* It is used in the paint manufacture and in the production of lead glass (p. 199) It melts easily, and when heated with hydrogen or carbon is converted into lead.

Minium, or *red lead,* Pb_3O_4, results from the protracted heating of litharge with air-access. It is a heavy, scarlet, crystalline powder which is used as a color. Its formula may be written thus:

$$PbO_2 2PbO.$$
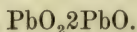
We may regard it, then, as a compound of lead oxide and lead dioxide. When it is treated with dilute nitric acid, the lead oxide is converted into lead nitrate, which is soluble and can be washed out with water, while *lead dioxide,* PbO_2, remains. This is a heavy, dark-brown powder, insoluble in water and in nitric acid. It yields up its additional oxygen readily, and when a little of it is ground in a mortar with some sulphur, the mixture is inflamed. Lead dioxide is part of the mixture of which the heads of matches consist.

Both lead dioxide and red lead are easily converted into lead oxide by heat, oxygen escaping.

Lead is quadrivalent in lead dioxide, and in lead tetrachloride, $PbCl_4$, a colorless, very unstable liquid. But all of its important compounds correspond to lead oxide, and in them the metal is bivalent. Almost all lead salts are insoluble in water, or nearly so, the only important exceptions being lead nitrate and lead acetate.

293. **Lead sulphide,** PbS, is the mineral *galenite,* or galena. It crystallizes in cubes, which have a lead-gray, metallic luster and are brittle. It is produced as a black precipitate when hydrogen sulphide is passed into a lead solution:

$$PbCl_2 + H_2S = PbS + 2HCl.$$
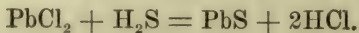
The insolubility of lead sulphide is almost complete, and the precipitate forms even in the most dilute lead solutions. This is therefore a very delicate test for lead.

Lead sulphate, $PbSO_4$, occurs in nature as the mineral *anglesite*. It is insoluble in water, and is formed as a heavy white precipitate when $\overset{=}{SO_4}$ ions and $\overset{++}{Pb}$ ions come into contact, e. g.:

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3.$$
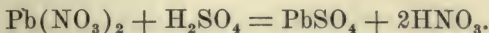
Lead chloride, $PbCl_2$, is only slightly soluble in cold water and is precipitated when chlorine ions and lead ions come together, unless the solution is dilute. It is white, and is much more soluble in hot water than in cold.

Lead carbonate is white, and insoluble in water. It occurs in nature as the mineral cerussite.

A substance containing lead hydroxide and lead carbonate in about the proportions expressed by the following formula,

$$Pb(OH)_2 2PbCO_3,$$
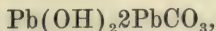
is called **white lead.** In spite of its active poisonous qualities, it is the most common of white pigments, and is the basis of most ordinary paint.

CHAPTER XXX

THE NITROGEN GROUP

Nitrogen, N.	Antimony, Sb.
Phosphorus, P.	Bismuth, Bi.
Arsenic, As.	

294. We have here an example of the fact that, in the same group, the metallic properties usually increase with the atomic weight. Nitrogen ($N = 14$) and phosphorus ($P = 31$) are non-metals, arsenic ($As = 75$) and antimony ($Sb = 120$) are metalloids, bismuth ($Bi = 208$) is a metal. Nitrogen, phosphorus, arsenic, and antimony each form a gaseous compound with hydrogen of the formula RH_3 (R being an atom of the element in question). The stability of these compounds decreases in the order in which the elements have been named, with increasing atomic weight. No compound of bismuth with hydrogen has been obtained. The elements of this group are trivalent or quinquivalent. Compounds in which they exhibit other valences are known, but they are exceptional.

PHOSPHORUS, P = 31.

295. **History.**—Phosphorus was discovered in the latter part of the seventeenth century by Brand, an alchemist, who was attempting to prepare a liquid which would turn silver into gold. In this search he had occasion to evaporate urine to dryness and heat the residue strongly, and obtained phosphorus among the products which condensed. On account of its inflammability and its luminosity in the dark,

the substance excited great wonder, and was exhibited to various princes, among others to Charles II of England. Here Boyle made its acquaintance, and soon after worked out for himself the same method of making it; but the process was tedious and the yield very small, and phosphorus remained a curiosity until, about a century after its discovery, Scheele pointed out that the ashes of bones contained it in abundance.

296. **Occurrence.**—Phosphorus does not occur free in nature. It is found only as the salts of its most important acid, *phosphoric acid,* H_3PO_4. These salts are called *phosphates,* and calcium phosphate, $Ca_3(PO_4)_2$, is abundant. It is contained in many minerals and rocks, and in all fertile soils. From the soil phosphorus compounds pass into plants; cereals especially are quite rich in them. The bones and teeth of mammals are largely calcium phosphate, and brain and nerve tissue always contain considerable quantities of complex phosphorus compounds.

297. **Preparation.**—The raw material for the preparation of phosphorus is calcium phosphate, $Ca_3(PO_4)_2$. This is used either as bone-ash, which is mainly calcium phosphate, or as the *phosphate rock,* which occurs naturally. It is mixed with charcoal powder and fine sand, and heated to a high temperature by means of the electric arc which burns between carbon rods projecting into the mixture. Phosphorus is liberated as vapor which is condensed under water.

298. **Properties.**—Phosphorus obtained in this way is a colorless, transparent solid, brittle when very cold, but at ordinary temperatures soft enough to be cut with a knife. It is insoluble in water but freely soluble in carbon disulphide. When phosphorus is sealed up in a glass tube from which the air has been removed, and allowed to stand in a dark place, it slowly vaporizes and condenses on the sides of the tube in well-developed transparent crystals. The phosphorus of commerce—usually in sticks or spheres

15

—has a crystalline structure, but a confused one, no crystal having had space and time to develop.

Phosphorus burns brilliantly to phosphoric oxide, also called phosphorus pentoxide, P_2O_5, when heated gently in the air, and often takes fire spontaneously. At ordinary temperatures it oxidizes slowly, and this oxidation is accompanied by the production of ozone and by the evolution of light which is visible in the dark. Phosphorus is not luminous when placed in hydrogen or any other gas which contains no free oxygen.

Nor is it luminous in pure oxygen. If a stick of phosphorus is transferred in the dark from a jar of air (in which, of course, it is giving off light) into a jar of oxygen, the luminosity is quenched at once. But the phosphorus begins to shine again when some of the oxygen in the jar is removed by an air-pump until the pressure of that which is left is about $\frac{1}{5}$ of an atmosphere—in other words, when the jar contains only about the same quantity of oxygen as the same volume of air. In this way it can be shown that when phosphorus is placed in a vacuum and oxygen admitted, it begins to shine as soon as the vessel contains any oxygen at all, and that the shining ceases when the pressure of the oxygen has reached a certain amount. The higher the temperature the greater the pressure required to stop the shining, so that phosphorus which has ceased to be luminous, owing to too much oxygen in the vessel, again becomes so when the temperature is slightly raised.

299. **Effect on the system.**—Phosphorus is intensely *poisonous,* and on account of the ease with which it can be obtained from the heads of matches is frequently made use of by criminals. There is also a chronic phosphorus poisoning which is frequent among workmen in match-factories, who come in daily contact with the substance. Two of the results are a replacement of the muscular tissue of certain parts of the body by fat (notably the heart) and a distressing decay of the bones of the jaw.

300. **Red phosphorus.**—This is a dull red powder of imperfect crystalline structure. It is not luminous in the

dark, and its oxidation in the air is immensely slower than
that of the colorless variety. Further, the temperature at
which it ignites is much higher. This is well shown by
putting a small quantity of each modification on a flat brass
rod, a few inches apart, and heating the rod in such a way
that the red phosphorus is nearest
the burner-flame (Fig. 39). The
colorless phosphorus will be the first
to inflame. Red phosphorus is in-
soluble in carbon disulphide and the
other liquids which dissolve the white
variety. Red phosphorus is not poi-
sonous at all when swallowed, but if
it is suspended in water and the liquid
injected into a vein, phosphorus-poi-
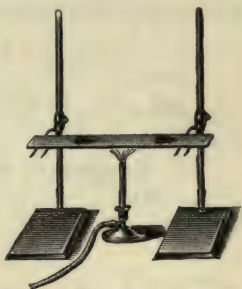soning results.

Fig. 39.—Proof that red phos-
phorus is less inflammable
than colorless phosphorus.

301. **Proof that red and white
phosphorus are two forms of the same element.**—Why do
we regard two bodies so totally unlike as two forms of the
same substance? For two reasons chiefly: First, because
we can transform either completely into the other without
adding or subtracting anything except energy; second, be-
cause they both react with the same elements to form the
same products. Thus both burn in oxygen, and the phos-
phoric oxide prepared in this way from colorless phosphorus
is identical with that from the red variety.

Colorless phosphorus is unstable and is continually pass-
ing into red phosphorus, which is the natural state of the
element, but this change is very slow, so that it may be
kept for years without any great alteration. Light quick-
ens the change, and when a bottle containing sticks of
phosphorus has stood for a long time in the same position,
that side of each stick which is struck by the light becomes
covered with a film of red phosphorus. But the best means
of accelerating the change is heat, and red phosphorus is

made by heating the colorless variety to 260° for about ten days in iron vessels, from which the air is excluded to prevent combustion.

302. **Uses of phosphorus.**—The chief use of phosphorus is for the production of matches. The match-sticks are first dipped into melted paraffin to make them inflame more easily, and then into a paste which contains phosphorus with lead dioxide, PbO_2, or some other substance rich in oxygen, and glue, to hold the mass together. They are then dried.

303. **Compounds of phosphorus and hydrogen.**—*Phosphine,* PH_3, is made by heating colorless phosphorus with
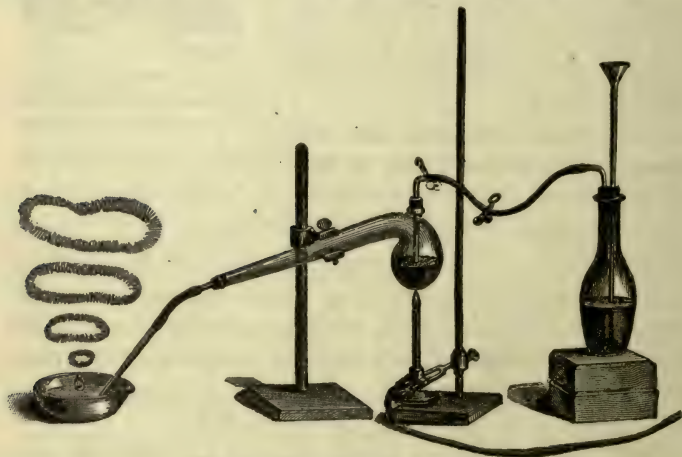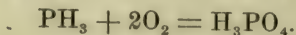

Fig. 40.—Preparation of phosphine.

a solution of sodium hydroxide. The air must all be expelled beforehand from the retort by a current of hydrogen or illuminating gas, and the exit tube must dip under warm water (Fig. 40). Colorless bubbles rise through the water in the dish and inflame spontaneously, producing white smoke-rings of phosphoric acid, H_3PO_4:

$$PH_3 + 2O_2 = H_3PO_4.$$

Pure phosphine is a colorless, poisonous gas with an odor like that of decaying fish. It corresponds in composition to ammonia, NH_3 (p. 105), and we should expect it, like the latter, to unite with acids yielding salts corresponding to the ammonium salts. For instance, we should expect reactions like this—

$$PH_3 + HCl = PH_4Cl—$$
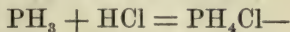
to occur. This compound PH_4Cl corresponds to ammonium chloride, and is called *phosphonium chloride*. It is very unstable and can only exist at temperatures far below 0°. On the other hand, *phosphonium iodide*, PH_4I, is well known and stable.

Pure PH_3 does not inflame spontaneously. If the gas, made as described above, is allowed, before escaping into the air, to pass through a U-shaped tube immersed in a freezing mixture, there condenses in this tube a colorless liquid, and the phosphine which escapes no longer takes fire of itself, though it is still very inflammable. Clearly the liquid which collects in the U-tube must be the cause of the spontaneous ignition, and this we can prove by opening the tube cautiously, when the liquid inflames and continues to burn with a bright flame, producing a dense white smoke. The liquid which collects in the tube is another compound of hydrogen and phosphorus. It corresponds to hydrazine, and has the composition P_2H_4.

CHAPTER XXXI

### OXIDES AND ACIDS OF PHOSPHORUS—HALOGEN COMPOUNDS

304. *Phosphorous oxide,* P_4O_6, is obtained as a white volatile powder, with a garlic odor, by burning phosphorus in a limited supply of air. It burns, when heated in air or oxygen, to

Phosphoric oxide, also called *phosphorus pentoxide,* P_2O_5. This is the product of the combustion of the element when the supply of oxygen is plentiful. It is a loose, white, odorless powder with an acid taste. Its attraction for water is extraordinary, and the best means of drying a gas is to allow it to stand for a time in contact with this substance.

305. **Acids containing phosphorus.**—When phosphorus pentoxide is thrown into water it dissolves with a hissing noise, and the liquid becomes hot. Combination has taken place, and the solution contains *metaphosphoric acid,* HPO_3—

$$P_2O_5 + H_2O = 2HPO_3.$$
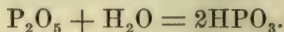
The metaphosphoric acid can be obtained, as a glassy mass, by evaporating the solution to dryness and heating the residue. But if the solution be allowed to stand, the metaphosphoric acid combines with more water and passes into *phosphoric acid,* H_3PO_4—

$$HPO_3 + H_2O = H_3PO_4.$$
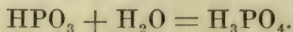
Phosphoric acid is the most important acid of phosphorus. It forms hard, brittle, colorless crystals, very solu-

216

ble in water. The salts of this acid, the *phosphates,* are the only compounds of phosphorus found in nature. Phosphoric acid contains three atoms of hydrogen which can be replaced by metals, and therefore each metal can form three phosphates, e. g.:
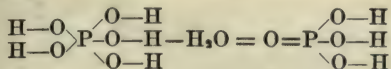
(1) NaH_2PO_4, monosodium phosphate;
(2) Na_2HPO_4, disodium phosphate;
(3) Na_3PO_4, trisodium phosphate;

while with a bivalent metal, like calcium, the corresponding salts will be

(1) $Ca(H_2PO_4)_2$;
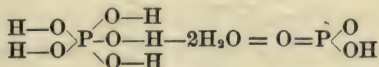(2) $CaHPO_4$; and
(3) $Ca_3(PO_4)_2$.

Salts of the first type are soluble in water. Those of the second and third are insoluble in it, except with potassium and sodium, all of whose salts are soluble. All of the phosphates are soluble in nitric acid except tin phosphate.

A hydroxide in which phosphorus is quinquivalent would have the formula $P(OH)_5$. This compound is unknown, but phosphoric acid may be looked upon as derived from it by the loss of a molecule of water; thus

$$\begin{matrix} H-O \\ H-O \end{matrix} \Big> P \begin{matrix} O-H \\ -O-H \\ O-H \end{matrix} - H_2O = O=P \begin{matrix} O-H \\ -O-H \\ O-H \end{matrix}$$

<div align="right">Phosphoric acid.</div>

Metaphosphoric acid can be regarded as derived from the same hydroxide by the loss of two molecules of water:

$$\begin{matrix} H-O \\ H-O \end{matrix} \Big> P \begin{matrix} O-H \\ -O-H \\ O-H \end{matrix} - 2H_2O = O=P \begin{matrix} O \\ OH \end{matrix}$$

<div align="right">Metaphosphoric acid.</div>

The hydroxide in which phosphorus is trivalent is called *phosphorous* acid, $P(OH)_3$. It can be obtained by treating phosphorus trichloride, PCl_3, with water—

$$PCl_3 + 3H_2O = P \begin{matrix} O-H \\ -O-H \\ O-H \end{matrix} + 3HCl.$$
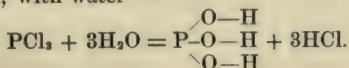
It is a colorless, crystalline, deliquescent solid, which tends constantly to absorb more oxygen and pass into phosphoric acid.

A number of other substances containing phosphorus, hydrogen, and oxygen is known. These substances are all acids, and are more or less similar to those we have discussed.

306. **Compounds of phosphorus and sulphur.**—Four compounds of these two elements have been made by heating
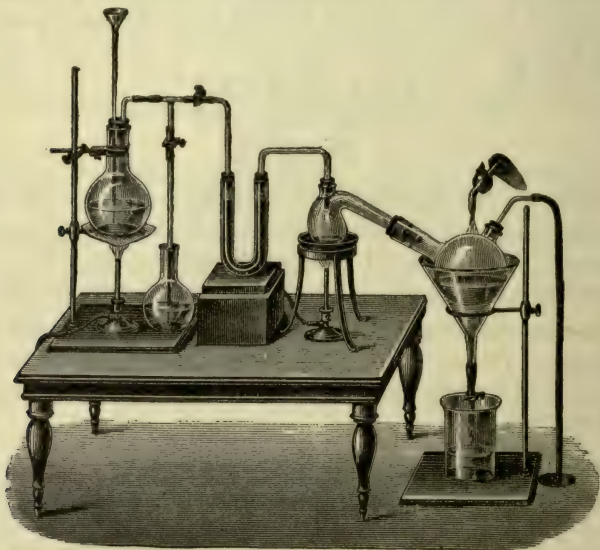

FIG. 41.—Preparation of phosphorus trichloride.

them together in vessels from which the air has been expelled by a current of carbon dioxide. Red phosphorus must be employed, for explosions occur when the colorless variety is used. The compound corresponding to phosphorus pentoxide is *phosphorus pentasulphide,* P_2S_5. It forms yellow crystals, which melt and vaporize without decomposition if air is excluded. If not, they take fire and burn with a pale flame. This substance is of frequent use in the chemistry

of the carbon compounds, for when it acts upon them it frequently removes the oxygen and inserts sulphur in its place. Thus, when alcohol, C_2H_6O, is treated with it, the corresponding sulphur compound, called mercaptan, C_2H_6S, is obtained.

The other sulphides of phosphorus are similar to phosphorus pentasulphide.

307. **Compounds of phosphorus with chlorine.**—When phosphorus is melted in a retort and a current of chlorine passed over it, it burns with a pale flame, and *phosphorus trichloride,* PCl_3, passes off as a vapor, which can be condensed by cooling (Fig. 41). It is a colorless liquid with a pungent odor. The vapor attacks the eyes, causing tears. Its behavior with water has just been discussed. When exposed to air, it slowly absorbs oxygen, passing into *phosphorus oxychloride,* $POCl_3$, which resembles it very closely. When more chlorine is allowed to act upon phosphorus trichloride, combination takes place and *phosphorus pentachloride,* PCl_5, is produced in white, lustrous crystals.

ARSENIC, As = 75.

308. Occurrence.—Native arsenic is rather widely distributed. Compounds of the element also occur. Important among these is iron sulph-arsenide, FeSAs, from which arsenic can easily be obtained by heating and condensing the vapor which is given off:

$$FeSAs = FeS + As.$$
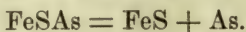
Many of the metallic sulphides which are important as ores contain arsenic. When such ores are roasted to produce the oxides, from which the metals are afterward to be extracted, the arsenic burns to arsenious oxide, As_4O_6, which is a frequent by-product in such operations. Minute traces of arsenic are contained in animal tissues—for instance, in the human thyroid gland, skin, and hair. The entire human body contains about half a milligram of the element.

309. Properties.—Arsenic exists in several modifications. When arsenic vapor is suddenly cooled it condenses to a yellow powder, which oxidizes readily in the air, dissolves in carbon disulphide, and in many respects exhibits similarity to colorless phosphorus. It is unstable and easily passes into crystallized arsenic. There is also a black amorphous variety which is much more stable and more easily obtained than the yellow. Crystallized arsenic is nearly tin-white, with a metallic luster, brittle, and easily powdered. When heated under the ordinary pressure of the air, arsenic vola-

tilizes without melting, but it may be melted under strong pressure. The vapor is lemon-yellow and poisonous. Its density, referred to hydrogen, is 150. Therefore, the molecular weight must be $150 \times 2 = 300$. Accordingly, the formula of arsenic is As_4; there are four atoms in the molecule.

310. **Arsine,** AsH_3, corresponds to ammonia. It can be obtained pure by treating sodium arsenide (made by heating sodium and arsenic together) with hydrochloric acid:
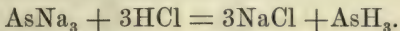
$$AsNa_3 + 3HCl = 3NaCl + AsH_3.$$
Sodium arsenide.

Arsine is a colorless, unpleasant-smelling gas which has been condensed to a transparent liquid. A temperature approaching redness separates it into hydrogen and arsenic. It is combustible, burning to water and arsenious oxide. Arsine is frightfully poisonous, and the greatest care is required in working with it. Even traces of it in the air cause dizziness, breathlessness, and fainting.

When a solution of arsenious oxide, or some other arsenic compound, is added to a liquid in which hydrogen is being generated, arsine is produced, and escapes mixed with the hydrogen: [1]

$$As_4O_6 + 24H = 4AsH_3 + 6H_2O.$$

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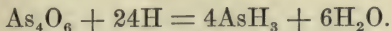
[1] On the other hand, if the hydrogen is generated in another vessel and passed into the arsenic solution through a glass tube, there is no action. Thus it will be seen that hydrogen, in the moment of its liberation, can cause a chemical change which free hydrogen, ready formed, is powerless to effect. Here is another example: If silver chloride is suspended in water, and hydrogen passed through the water, nothing occurs; but if zinc and sulphuric acid, or any other substances which can generate hydrogen, are added to the *same liquid,* the silver chloride is rapidly converted into metal:

$$AgCl + H = HCl + Ag.$$

From the standpoint of the atomic theory, such behavior is explained by the statement that hydrogen is first liberated as atoms. Afterward

This operation can be conducted in the apparatus represented in Fig. 42. Zinc and dilute sulphuric acid are placed in the generator, and when hydrogen is being evolved in a regular stream, a few drops of a water solution of arseni-
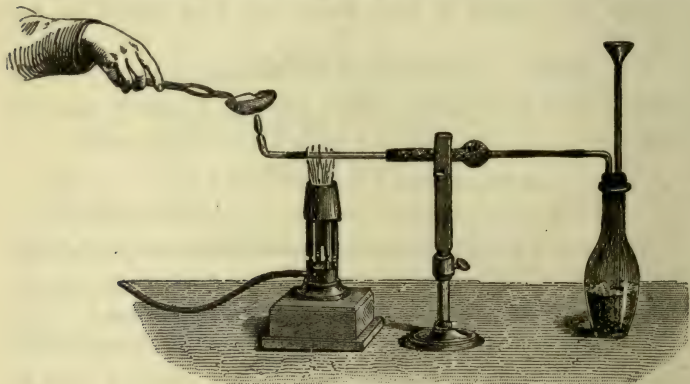

Fig. 42.—Marsh's test.

ous oxide are added through the funnel-tube. The colorless hydrogen flame, burning at the jet, enlarges, becomes violet-gray, and gives off a white smoke of arsenious oxide from the combustion of the arsine. If the flame is cooled by placing a porcelain dish in it, arsenic condenses in blackish-brown spots on the dish.

If the tube through which the mixture of hydrogen and arsine passes is heated by a burner flame, the arsine is decomposed by the heat and a steel-gray mirror of arsenic forms in the tube. The formation of this mirror is a marvelously delicate method of detecting the presence of arsenic, and is much used in cases of suspected poisoning. It is called, after its discoverer, *Marsh's test.*

these unite to form molecules, H_2, and then they become less energetic, because the bond between the two must be ruptured before any chemical action can occur. This condition of activity at the moment of production is called the *nascent state*, and many similar cases are known, not only with hydrogen, but with other elements.

311. **Arsenious oxide,** As_4O_6, occurs in commerce as a dense, white crystalline powder. By slowly cooling its vapor it can be obtained in a glassy, amorphous modification, which becomes opaque and white on being preserved, passing into an aggregate of small crystals.[1] Arsenious oxide dissolves very slowly in water in the cold, but considerable quantities of it will dissolve if time enough be given. It is often called white arsenic, or simply arsenic. It is highly poisonous, and owing to the ease with which it can be obtained and to the fact that its taste is very feeble, it is more frequently employed by poisoners than any other substance. The poisons of the Borgias and the famous " Acqua Toffana," with which, it is said, six hundred persons were slain, were in all probability preparations containing arsenious oxide.

312. *Arsenic pentoxide,* As_2O_5, corresponding to P_2O_5, is a white solid which dissolves in water, producing arsenic acid, H_3AsO_4, corresponding to phosphoric acid, H_3PO_4. The salts of arsenic acid, the arsenates, strongly resemble the phosphates, and usually crystallize in the same forms. They are mostly insoluble in water, but those of the metals of the sodium group are soluble.

313. Three sulphides of arsenic have been made by melting together the two elements in the proper proportions.

Arsenic disulphide, As_2S_2, is red, crystalline, and transparent. It was formerly used as a paint under the name *realgar.*

Arsenic trisulphide, As_2S_3, is yellow, and is still occasionally used as a color. When hydrogen sulphide is passed into a solution of arsenious oxide in water, the liquid turns

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[1] The amorphous arsenious oxide is more soluble in water than the crystalline. In fact, different modifications of the same solid always have different solubilities in the same liquid, the unstable form being the more soluble.

deep yellow, but remains clear. Arsenic trisulphide has been formed thus:

$$As_4O_6 + 6H_2S = 2As_2S_3 + 6H_2O;$$
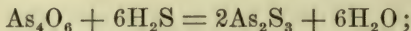
but though insoluble in water when once formed, it does not precipitate, but remains in the liquid in a curious state intermediate between solution and suspension. This condition is called *colloidal solution*. It is different from a suspension in passing through a filter without leaving any solid matter upon it, and in being apparently clear. Many other colloidal solutions are known. They behave like suspensions in which the suspended substance is very finely divided.

The addition of a few drops of hydrochloric acid will cause the arsenic trisulphide to separate in yellow flakes, and it is now entirely insoluble.

Arsenic pentasulphide, As_2S_5, is yellow and unstable, tending to separate into arsenic trisulphide and sulphur.
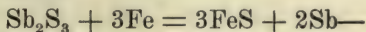
THE NITROGEN GROUP (Continued)

ANTIMONY AND BISMUTH

ANTIMONY, Sb = 120.

314. Preparation.—Antimony occurs native, but its most important ore is the sulphide Sb_2S_3, which is called *stibnite*. From this the element is obtained by strongly heating with iron filings in a well-covered crucible—

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb—$$

or by carefully roasting the sulphide in a furnace until it is converted into antimony oxide. This is then mixed with powdered coal, or some other form of carbon, and heated to faint redness, when carbon dioxide escapes and antimony remains.

315. Properties.—Antimony is a crystalline, brittle substance with a silver-white, metallic luster. It melts easily and volatilizes at a strong red heat. It is not affected by air at ordinary temperatures, but when heated burns, giving off a white smoke of antimonious oxide, Sb_4O_6. The element is employed in the production of several important alloys. Type metal is an alloy of lead, tin, and antimony; Britannia metal an alloy of antimony and tin.

316. Stibine, SbH_3, resembles arsine, and is made by similar methods—e. g., by treating an alloy of zinc and antimony with hydrochloric acid:

$$Sb_2Zn_3 + 6HCl = 3ZnCl_2 + 2SbH_3.$$
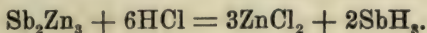
It is a colorless gas with an unpleasant odor, less poisonous than arsine. It is very unstable, separating into its constituents even at ordinary temperatures and rapidly when heated. For this reason it has never been obtained pure, and our knowledge of its properties has been obtained by studying a mixture of the gas with hydrogen. If a solution of an antimony compound is added to the contents of a hydrogen generator, as in Marsh's test (p. 222), stibine escapes, mixed with the hydrogen. If the tube through which the gas passes is heated the stibine is decomposed and an *antimony mirror* is deposited. Or, if a cold porcelain dish is held in the flame of the burning gas, *antimony spots* are formed upon it. These deposits of antimony are not affected by a solution of sodium hypochlorite, $NaClO$, which rapidly dissolves the arsenic mirror and spots, and this fact enables us to decide which element is present.

317. We have pointed out that in the same group the elements usually become more metallic with increasing atomic weight. We should therefore expect antimony to be more metallic than arsenic. That this is the case is shown by the fact that antimony is able, to a small extent, to replace the hydrogen of acids forming salts. Arsenic is not. Thus, antimony sulphate, $Sb_2(SO_4)_3$, and antimony nitrate, $Sb(NO_3)_3$, are known, but they are very unstable.

The formula of stibine, SbH_3, shows that antimony is trivalent toward hydrogen. The valence of an element toward hydrogen is always the same. Thus, if a compound SbH_5 were obtained, we should have to admit that antimony could have a valence of five as well as three toward hydrogen. Such cases are unknown. However, antimony is both trivalent and quinquivalent toward the halogens, and almost all the compounds SbX_3 and SbX_5 (where X is a halogen atom) are known.
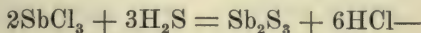
Antimony trisulphide, Sb_2S_3, is the mineral stibnite. It occurs in brittle, heavy, blackish-gray crystals, which melt

JUSTUS VON LIEBIG

B. Germany, 1803.　D. Munich, 1873.

easily, even in the flame of a candle. The antimony trisulphide obtained by precipitating an antimony solution with hydrogen sulphide—

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl—$$

is an orange-red, amorphous powder, totally different from stibnite, but having the same composition. It can be obtained gray, metallic, and crystalline, like stibnite, by melting it and letting it cool slowly.

BISMUTH, Bi = 208.

318. Bismuth occurs in nature chiefly as metal. Compounds of the metal are found also, but only the *sulphide*, "bismuth glance," Bi_2S_3, possesses any importance as an ore. The usual ores contain bismuth, more or less bismuth sulphide, and other substances. They are first roasted, which burns away the arsenic which is usually present, and converts much of the bismuth sulphide into bismuth trioxide, Bi_2O_3. The roasted ore consists, therefore, of a mixture of bismuth, bismuth trioxide, and unaltered bismuth sulphide, together with the earthy or stony impurities called by the miners "gangue." It is mixed with carbon and iron filings and melted in crucibles. The carbon removes the oxygen from the bismuth oxide, and the iron the sulphur from the bismuth sulphide, producing in both cases bismuth, which mixes with that which was present at the beginning, and which, of course, is melted by the heat. The metal collects in a layer on the bottom of the crucible.

Bismuth has a strong, reddish-white metallic luster and forms crystals which look like cubes but are not, because measurement shows the angles to be oblique. It melts very readily (270°), and its alloys melt at still lower temperatures. An intimate mixture of two substances in the proper proportions always melts at a lower temperature than either alone, provided that on being melted they form a solution.

16

Thus, the melting-point of ice is not affected by mixing it with sand, which does not dissolve in the water produced by the melting, but when the ice is mixed with salt, which does dissolve, the ice melts at a lower temperature. Metals behave in the same way, and bismuth is used, along with cadmium, tin, and lead in the manufacture of fusible alloys, some of which melt easily in hot water (p. 179).

Bismuth burns to Bi_2O_3, when heated in the air. Hydrochloric acid does not affect it. Hot, strong sulphuric acid converts it into sulphate. Nitric acid, either cold or hot, dissolves it easily to bismuth nitrate, $Bi(NO_3)_3$.

Bismuth is usually trivalent. No compounds are known in which one atom of bismuth combines with five halogen atoms.

Bismuth nitrate, $Bi(NO_3)_3$, results when the metal is dissolved in nitric acid. When the liquid is evaporated it forms colorless crystals which contain five molecules of water. Like other bismuth salts, the nitrate is decomposed by water,

$$Bi(NO_3)_3 + H_2O = BiONO_3 + 2HNO_3,$$
Bismuth oxynitrate
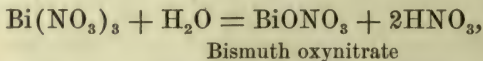
bismuth oxynitrate being deposited as a white powder insoluble in water. This powder is largely used in medicine under the name " subnitrate of bismuth."

Bismuth has a remarkable tendency to form compounds, like $BiOCl$ and $BiONO_3$, which are partly salts and partly oxides. Such compounds are called *" basic salts."* Sometimes a basic salt is written simply as a compound of the salt itself with the oxide. Thus, basic lead chloride may be written $PbCl_2.PbO$. A compound which is partly salt and partly hydroxide is also called a basic salt. Thus, tin basic chloride is $Sn{Cl \atop OH}$.

CHAPTER XXXIV

THE CHROMIUM GROUP

Chromium, Cr.   Uranium, U.

CHROMIUM, Cr = 52.

319. Chromium and uranium are metals, but they have one important non-metallic characteristic—they form part of the make-up of acids. Thus, chromium forms an acid, H_2CrO_4 (known chiefly in its salts), and similar compounds of uranium are known. H_2CrO_4 is called *chromic acid,* and its salts, the *chromates,* exhibit many similarities with the sulphates.

320. Occurrence and preparation.—Chromium has not been found free in nature. Its most abundant compound is *chromite,* or chrome iron ore, which may be regarded as a double oxide of iron and chromium, $Cr_2O_3.FeO$. This is the source of the chromium compounds of commerce.

For a century after the discovery of the element (1797) the preparation of chromium was difficult, but within the last few years two excellent methods of making it have been devised which bid fair to become of commercial importance.

First, when chromic oxide, Cr_2O_3, is heated with carbon to the temperature of the electric arc, carbon monoxide escapes and chromium is produced.

Second, when a mixture of chromic oxide and powdered aluminium is strongly heated at one point the whole sub-

stance becomes intensely white-hot and is converted into aluminium oxide and chromium:

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr.$$
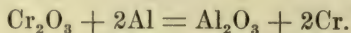
321. Properties.—Chromium is a metal with a grayish-white luster which is only slightly tarnished in the air. It is soft enough to be easily filed, and is not attracted by the magnet. It does not melt in the oxyhydrogen flame. At a high temperature it burns in oxygen to Cr_2O_3, producing sparks like those of burning iron, but more brilliant.

322. Peculiar behavior toward acids.—Hydrochloric acid dissolves chromium, liberating hydrogen, and it frequently happens that, when the chromium is first dropped into the acid, the action is very slow, but gradually gathers strength until it is quite energetic, then diminishes until scarcely any hydrogen is liberated, then again increases, and so on until the chromium is all dissolved. If chromium is left exposed to the air it gets into what is called the *passive state*, in which it behaves like gold and is insoluble in acids. But if the chromium, while under the acid, is touched with a piece of zinc, the passive state is destroyed, hydrogen is liberated, and the chromium suddenly begins to dissolve.

323. *Chromic oxide*, Cr_2O_3, can be obtained by heating the hydroxide. When amorphous it is bright green, when crystallized blackish-green. It is insoluble in acids and not affected by any ordinary heat. Under the name " chrome green " it is used for painting on porcelain.

When, in a series of salts, a metal has the same valence that it has in a certain oxide, we are in the habit of saying that the salts *correspond* to or are *derived* from that oxide. Thus the common salts of lead, like $PbCl_2$ and $Pb(NO_3)_2$— in which the lead is bivalent—correspond to litharge PbO, and not to PbO_2 or Pb_3O_4. In this sense the ordinary salts of chromium—the chromic salts—are derived from chromic oxide, for in both the oxide and the salts the metal is trivalent.

324. *Chromic chloride*, $CrCl_3$, forms green crystals with

$6H_2O$, which are quite soluble in water. Anhydrous $CrCl_3$ forms violet-red scales, which are practically insoluble in water—a remarkable fact, for we should expect the scales to combine with water, producing $CrCl_36H_2O$, and then dissolve.[1]

The other chromic salts, the sulphate, nitrate, and so on, exhibit the same curious insolubility of the anhydrous salt.

325. Chromium trioxide, CrO_3, is made by decomposing a solution of *potassium dichromate*, $K_2Cr_2O_7$, with sulphuric acid:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3.$$
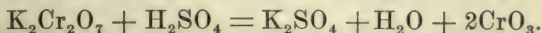
It crystallizes in red needles, which are deliquescent and very soluble in water. When heated gently it melts without decomposition, but at a higher temperature it separates into chromic oxide and oxygen. Formerly it was called by the incorrect name of "*chromic acid,*" and this name is still in use in commerce.

326. Chromic acid, H_2CrO_4, is obtained in small rose-red crystals by cooling a saturated solution of chromium trioxide in water. It is very unstable, easily separating into CrO_3 and H_2O. Its salts, on the other hand, are well known and stable. They are called the chromates. Chromic acid corresponds to sulphuric acid H_2SO_4, and the chromates correspond to the sulphates. The sulphate and the chromate of the same metal usually crystallize in the same form.

Potassium chromate, K_2CrO_4, forms yellow crystals, soluble in water to a yellow liquid.

Lead chromate, $PbCrO_4$, is made by adding a solution of potassium chromate (or of potassium dichromate) to a solution of a lead salt, thus:

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2KNO_3.$$

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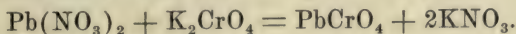
[1] The explanation is that the speed with which anhydrous $CrCl_3$ dissolves is very small. In presence of certain substances, which act catalytically, it dissolves rapidly.

Most of the chromates of the metals are yellow or red. Many of them are insoluble in water.

327. Potassium dichromate, $K_2Cr_2O_7$, is made from chrome iron ore by various methods, one of which is to heat the powdered mineral with potassium carbonate in a current of air. It serves as the starting-point for the preparation of other chromium compounds. At present the chromate and dichromate of sodium are replacing the potassium salts in commerce, because they are cheaper.

The dichromates are mostly red, and soluble in water.

Their composition can be remembered by imagining them to consist of the chromate with CrO_3. Thus potassium dichromate can be written $K_2CrO_4CrO_3$. There is also a potassium trichromate, $K_2CrO_4 2CrO_3$, and a potassium tetrachromate, $K_2CrO_4 3CrO_3$.

All of the chromium compounds are poisonous. The chromates and dichromates are more poisonous than the salts in which chromium acts like a metal.

328. Uranium is comparatively rare. It has a special interest because it has the highest atomic weight of all the elements known at present $(U = 239)$. It is found in nature chiefly as the mineral pitchblende, which is an oxide of the composition U_3O_8—usually very impure. The best method of making uranium is to heat purified U_3O_8 with pure charcoal to the temperature of the electric arc. It is a metallic substance with a pure white luster, non-magnetic, and soft enough to be filed.

When a piece of uranium or of pitchblende is placed in the dark near a photographic plate, and the plate is afterward developed, it is found to be affected in somewhat the same way as if the uranium had been a source of light during the time of exposure. Uranium and its compounds, then, have the power of sending forth rays which affect the photographic plate. But these rays differ from light in many remarkable ways. Thus, they pass readily through black paper and through thin plates of aluminium or copper. A thick plate of platinum or, best of all, a plate of lead will stop them. Again, the rays pass through a glass prism without being bent out of their

course, and are not reflected from a polished metallic surface in the same way as light. It has been shown that these curious rays are not due to the uranium itself, but to other elements which are contained in the pitchblende in small quantities. *Radium* (p. 171) is the most important of these elements.

The question how the radium compounds obtain the *energy* which they continuously give out is an unsolved riddle. A possible explanation is that the radium atom is not a single particle, but a group of numerous smaller particles, all in rapid motion. When the motion of a particle or group of particles becomes very energetic it separates from the rest of the atom and shoots out with great rapidity, producing the rays. At the same time the shock produces vibrations of the ether and the surrounding matter which appear as light and heat. What becomes of the rest of the radium atom after the fragment has been pitched off? It can no longer be radium. There is some evidence that the other product is *helium*—at least it appears that helium is constantly produced by radium compounds. This would realize the dream of the alchemists—the conversion of one element into another. But so far the evidence is not strong enough to establish such a revolutionary conclusion.

monoclinic or amorphous
white powder
plastic or soft.

crystal
rhombic
Monoclinic

CHAPTER XXXV

THE OXYGEN GROUP

Oxygen, O.   **Sulphur, S.**   **Selenium, Se.**   **Tellurium, Te.**

329. The elements of this group are non-metals. They all exist in several allotropic modifications. They combine with two atoms of hydrogen, and the products—except in the case of water, H_2O—are colorless gases with a foul odor and intense poisonous action. Oxygen has already been discussed. Sulphur is common. Selenium and tellurium are rare.

SULPHUR, S = 32.

330. **Occurrence and preparation.**—Large deposits of native sulphur occur in volcanic regions, particularly in Sicily, and most of the sulphur of commerce is obtained from this source. We have already seen that many sulphides—for instance, ZnS and PbS—are very important as ores of the metals. When such ores are roasted in order to convert the metal into oxide (afterward to be heated with carbon), the sulphur burns to sulphur dioxide, which is then converted into sulphuric acid and sold in this form.

A little of the sulphur of Sicily occurs in pure transparent yellow crystals, but the greater portion contains much calcium sulphate and earthy matter. The crude ore is piled in large heaps in shallow pits lined with plaster. These heaps are covered with powdered ore, and air-canals are left in the interior, so that the air has a limited access. Then the sulphur in the lower part of the air-canals is ignited, and a smothered combustion lasting some weeks ensues, during which nearly half of the sulphur is burned,

234

and the rest is melted by the heat and flows out. This burning of part of the sulphur in order to obtain the rest seems like a wasteful proceeding, but it must be remembered that fuel is scarce in Sicily, and the sulphur ore is the cheapest combustible at hand.
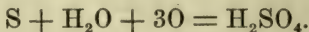
The crude sulphur obtained in this way still contains calcium sulphate, arsenic, and other substances. It is purified by distillation from cast-iron retorts, the vapor being led into a stone chamber, on the floor of which the melted sulphur collects. From time to time it is withdrawn and poured into cylindrical moulds of wood, in which it solidifies to form *roll sulphur*.

Flowers of sulphur is obtained by leading the sulphur-vapor into larger stone chambers, the walls of which remain cold. The sudden cooling condenses the vapor to a fine yellow powder, which is at first amorphous, but gradually becomes crystalline on being kept.

331. **Properties.**—Sulphur is a brittle yellow solid, and is practically a non-conductor of electricity and a very bad conductor of heat. It melts slightly above 100° to a thin, light yellow liquid. When this liquid is heated to a higher temperature it forms a jelly-like mass, darker in color, and so thick that the flask containing it can be inverted without the contents running down the walls. This thickening is accompanied by a distinct fall in temperature, which shows that another modification of sulphur, richer in energy, is formed. Heated still hotter, it again becomes a thin liquid, but is now reddish black and nearly opaque. Finally it boils. The vapor is at first yellow, but its color deepens with rising temperature until, at a faint red heat, it is blood-red. This variation in color would lead us to suspect that some alteration in the sulphur molecule occurs on heating. As a matter of fact, the density of the vapor shows that at low temperatures the formula is S_8, at high temperatures S_2. Sulphur is very soluble in carbon disul-

phide, CS_2, and in some other liquids, and it has been shown that the molecule of dissolved sulphur also contains eight atoms.

Heated in the air, sulphur takes fire and burns with a pale blue flame, mainly to sulphur dioxide, SO_2, but traces of sulphur trioxide, SO_3, are produced at the same time. Even at ordinary temperatures, sulphur oxidizes slowly in the air, and if some powdered sulphur is stirred up with water for a time and the mass poured upon a filter, sulphuric acid can be detected in the clear liquid which runs through:

$$S + H_2O + 3O = H_2SO_4.$$

Fig. 43.—Crystals of native sulphur.

332. Allotropic modifications. —Sulphur exists in a number of forms, most of which have not yet been carefully studied. Fig. 43 shows the form in which native sulphur crystallizes. Since native sulphur has remained as it is for unlimited years, it follows that this must be, at ordinary temperatures, the *natural state* of sulphur, the *stable form* to which all others change if time enough be given. We shall call this form *a*-sulphur.

That this is not the natural state of sulphur at slightly elevated temperatures we can show by heating one of the transparent crystals of *a*-sulphur in a corked test-tube, dry inside, and surrounded by boiling water. It slowly becomes opaque

Fig. 44.—β-sulphur.

and, while the form remains unchanged, the crystal is now a mass of prisms like that shown in Fig. 44, but very small. This *prismatic sulphur* we shall call β-sulphur. Large quantities of it can be made by melting sulphur in a crucible, letting it cool until a crust forms, piercing the crust, and pouring out the liquid interior. The inside of
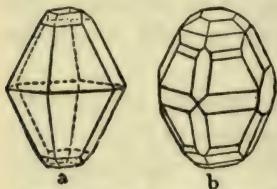
the crucible is lined with honey-yellow, transparent crystals shaped like Fig. 44, but elongated so as to form needles. If we allow the crucible to stand overnight, we find the crystals dull yellow and opaque. Each prism has changed to an aggregate of crystals like that shown in Fig. 43, but very minute, and while the prisms retain their form, they are now composed of a-sulphur, not of β-sulphur. In other words, β-sulphur in the cold behaves exactly as a-sulphur does when heated. Now since a-sulphur is the natural state in the cold and β-sulphur at 100°, there must be some temperature between at which the change of stability takes place. This temperature is 98°, and here a-sulphur, β-sulphur, and sulphur-vapor can exist in equilibrium, just as ice, liquid water, and water-vapor are in equilibrium at 0°.

There is also an amorphous form of sulphur, insoluble in carbon disulphide. This separates as a white powder when a solution of sulphur in carbon disulphide is exposed to sunlight or a beam of electric light.

When very hot liquid sulphur is suddenly cooled, *soft sulphur* is obtained. A good method of mak-

Fig. 45.—Preparation of soft sulphur.

ing it is shown in Fig. 45. The sulphur is distilled in the retort, and the hot liquid which condenses in the neck runs, in a thin stream, into cold water. Soft sulphur is a transparent mass which has somewhat the consistence of rubber, but is less tenacious. Its color varies from light yellow to dark brown. It is unstable, becoming brittle when kept, and changing to a mass of a-sulphur.
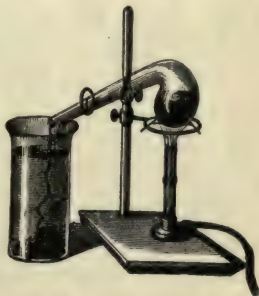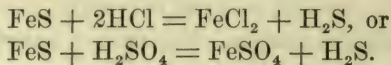
333. **Hydrogen sulphide,** H_2S.—When hydrogen is led into boiling sulphur the two elements combine to a slight extent, and traces of hydrogen sulphide are produced. The

compound is usually made by the action of dilute hydro-chloric or sulphuric acid on iron sulphide:

$$FeS + 2HCl = FeCl_2 + H_2S, \text{ or}$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Iron sulphide is easily obtained by melting iron and sulphur together. A grayish-black, metallic mass is formed, which is broken into lumps, placed in a gas-generating bottle, and covered with water. Hydrochloric or sulphuric acid is then poured through the funnel-tube, when hydrogen sulphide is at once evolved.

Hydrogen sulphide is a colorless gas with an odor resembling that of rotten eggs; in fact, the odor of rotten eggs is due to it, for during the process of decay the sulphur, which the albumin of the egg always contains, is liberated as H_2S. Hydrogen sulphide is somewhat soluble in water. It has been liquefied and solidified. When ignited it burns with a blue flame, the hydrogen to water, the sulphur to sulphur dioxide, and if a cold plate is introduced into the flame, the sulphur no longer burns, but is deposited as a yellow coating on the plate. Hydrogen sulphide is highly poisonous. Air containing less than $\frac{1}{10}$ of 1 per cent of it by volume is fatal to small animals.

Many of the sulphides of the metals are insoluble in water and are precipitated when hydrogen sulphide is passed into a liquid in which a salt of the metal is dissolved, thus:

$$CuCl_2 + H_2S = CuS + 2HCl.$$
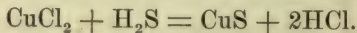
Many of these sulphides have characteristic colors. Zinc sulphide is white and antimony sulphide orange. Some are soluble in acids and are not precipitated until the acid in the solution is neutralized. For these reasons hydrogen sulphide is much employed by the chemist for detecting the metals and separating them from each other. On account of its unpleasant odor and poisonous qualities, various at-

tempts have been made to find a substitute for it, but it still remains a necessity in the analytical laboratory.

334. Hydrogen persulphide. —Another compound of hydrogen and sulphur is known. It is a yellow oil which spontaneously decomposes into H_2S and sulphur. Although it has been known for a century, we are still in doubt as to its composition. Very possibly its formula is H_2S_2, and it corresponds to hydrogen peroxide, H_2O_2. It is called *hydrogen persulphide.*
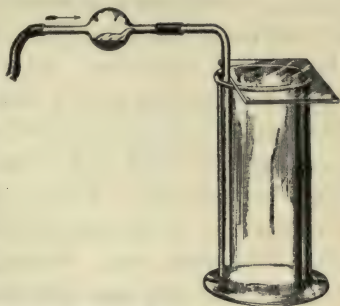

FIG. 46.—Preparation of sulphur dioxide from sulphur and oxygen.

335. Sulphur dioxide, SO_2, is the chief product when sulphur burns in the air or in oxygen. When sulphur is heated gently in a bulb-tube, through which a slow current

FIG. 47.—Proof that oxygen yields its own volume of sulphur dioxide.

of oxygen from a cylinder is passed, it burns with a blue, slightly luminous flame, and sulphur dioxide can be collected by downward displacement in a cylinder (Fig. 46).

Since the formula of oxygen is O_2, it is clear that when sulphur burns in oxygen no change in volume takes place, or, in other words, sulphur dioxide contains its own volume of oxygen. For let us suppose we have 32 grams of oxygen $= O_2 = 22.4$ liters. This will combine with 32 grams of sulphur, producing one molecular weight of $SO_2 = 64$ grams $= 22.4$ liters. That oxygen does produce an equal volume of sulphur dioxide when sulphur is burned in it can be shown by the experiment represented in Fig. 47. The

vessel in the figure is a small retort. At a is a small piece of sulphur. The liquid in the neck of the retort and in the trough below is mercury. The retort is filled with dry oxygen. Then a is heated gently with a burner until the sulphur takes fire. At first the level of the mercury sinks because the gas in the vessel is expanded by heat. Finally the sulphur flame is extinguished because the oxygen is all consumed, and, when the retort is cold, it is found that the mercury is at just the same level as before the combustion. In the language of the atomic theory, we may state this result thus: Every molecule of oxygen produces a molecule of SO_2, and therefore the total number of molecules is not altered by the combustion. Since equal volumes of gases contain equal numbers of molecules, the volume also must remain unchanged.

We have seen that when dilute sulphuric acid acts upon zinc, zinc sulphate is produced and hydrogen liberated. Copper behaves differently with sulphuric acid. The dilute acid does not act upon it, but hot strong sulphuric acid converts it into copper sulphate, liberating sulphur dioxide:

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$
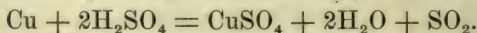
The copper may be heated with sulphuric acid in a flask, and the sulphur dioxide collected by downward displacement, the apparatus being arranged in the same way as for the production of chlorine (p. 76).

Sulphur dioxide is a colorless gas, with the suffocating odor of burning sulphur. It is easily converted into a colorless liquid by either cold or pressure, and the liquid freezes on further cooling. Water dissolves more than thirty times its volume of sulphur dioxide at ordinary temperatures. The solution is acid, and therefore must contain hydrogen ions. It is believed that the water and the sulphur dioxide unite to form a compound, H_2SO_3, which then dissociates thus:

$$H_2SO_3 = \overset{+}{H} + \overset{+}{H} + \overset{=}{SO_3}.$$
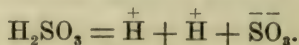
H_2SO_3 is therefore an acid, and the name *sulphurous* acid has been given to it. Sulphurous acid is only known in solution, but its salts, in which the hydrogen is replaced by metals, are stable and can readily be obtained. These salts are called the *sulphites*.

336. *Sodium sulphite,* Na_2SO_3, is the most important. It forms white crystals with $7H_2O$. It is largely used in photography, and to some extent also as a preservative. Thus, when added to fruit juices, like cider, it retards or altogether prevents the fermentation which would otherwise at once take place. However, the addition of any chemical product to articles of food is a dangerous operation and ought to be preceded by the most complete proof of the harmlessness of the substance added. Except those of the sodium group, the sulphites of the metals are insoluble in water.

337. **Sulphur trioxide,** SO_3.—Sulphur dioxide unites with oxygen, thus,

$$SO_2 + O = SO_3,$$
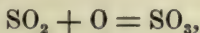
but the reaction is extremely slow. Certain substances, like finely divided platinum, or iron oxide, Fe_2O_3, cause the reaction to take place rapidly. Sulphur trioxide is made by leading a mixture of sulphur dioxide and oxygen over one of these substances at a gentle heat. In the laboratory, as well as on the large scale, asbestos covered with finely divided platinum is employed. This method of making sulphur trioxide is just now becoming of immense commercial importance. For the SO_3 produced when brought into contact with water yields sulphuric acid, H_2SO_4, and this way of making sulphuric acid bids fair to displace the older method.

Sulphur trioxide appears to exist in two modifications. One is a transparent liquid, which solidifies a little below room temperature. When this liquid is allowed to stand

it slowly passes into the second modification, a mass of white silky needles, resembling asbestos. Either form, when brought into contact with water, combines energetically with it, producing a hissing noise and great heat:

$$SO_3 + H_2O = H_2SO_4.$$
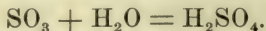
SO_3 is thus the *anhydride* of sulphuric acid, and can be called *sulphuric anhydride*.

338. **Sulphuric acid,** H_2SO_4.—When sulphur dioxide, air, and water are left in contact sulphuric acid is slowly produced—

$$SO_2 + O + H_2O = H_2SO_4—$$
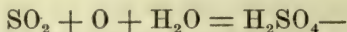
but the reaction is so slow that the acid could not be made practically by this method. But in presence of nitrogen peroxide, NO_2, the reaction becomes rapid. Chemists are still at odds over the *rôle* of the nitrogen peroxide. All that we can do here is to say that the action is a *catalytic* one (pp. 42–49), so that the nitrogen peroxide is not used up, but is able to produce large quantities of sulphuric acid, while remaining unchanged itself, and this statement about sums up the present knowledge of the matter.

339. **The lead-chamber process.**—This accelerating influence of nitrogen peroxide upon the combination of sulphur dioxide, oxygen, and water to sulphuric acid is the basis of the *lead-chamber process* for the manufacture of the acid. The sulphur dioxide is made by burning pyrite, FeS_2, when, according to the usual behavior of sulphides, the sulphur burns to SO_2 and the iron remains as Fe_2O_3. The combustion is so conducted that the SO_2 contains free oxygen from the air, which, as will be seen at once from the equation (paragraph 338), is necessary for the reaction which is to follow. The hot gases from the furnace are cooled and charged with nitrogen peroxide by methods which we shall not discuss. Then they pass into a large chamber built of thin plates of lead. The size of this chamber differs

·in different works. It may be 100 feet long, 20 feet wide, and 20 feet high. Into this chamber jets of steam from a boiler are passed, and here the combination of the sulphur dioxide, water, and oxygen takes place under the influence of the nitrogen peroxide, and the sulphuric acid falls in a fine rain to the floor. Through a short wide tube of lead the gases pass into a second similar chamber, and then into a third, to complete the reaction.

Since more steam is injected into the chambers than can take part in the reaction, the sulphuric acid contains water, usually about 35 per cent. Some of this water can be evaporated away by heating the acid in shallow lead pans, but when the evaporation has gone so far that the acid contains 80 per cent H_2SO_4 it begins to attack the lead and further evaporation must be conducted in vessels of platinum, which are plated inside with gold, for the strong acid acts somewhat even upon platinum.

This method of making sulphuric acid is carried out on an enormous scale. About four million tons of the acid are made by it yearly throughout the world, and nearly a million in the United States. But just at present it seems to be in serious danger of being abandoned in favor of the method spoken of just above (p. 241), in which sulphur trioxide is made first by passing SO_2 and oxygen over asbestos coated with powdered platinum, and then the SO_3 brought in contact with water. Already some of the largest works in the world have discontinued the lead-chamber process and adopted the new method.

340. **Properties.**—Pure sulphuric acid is a colorless oil which freezes at 10° to white crystals. When heated it boils at a high temperature (340°), but the suffocating vapor produced is not H_2SO_4. It is a mixture of sulphur trioxide and steam, for sulphuric acid decomposes when it is vaporized:

$$H_2SO_4 = H_2O + SO_3.$$

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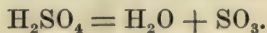
This we know from the density of the vapor. The mo-. lecular weight of sulphuric acid is 98.

$$2H = 2$$
$$S = 32$$
$$4O = 16 \times 4 = 64$$
$$\overline{98}$$

Hence if the vapor was H_2SO_4 its density referred to hydrogen would be $\frac{98}{2} = 49$.

But if it is separated into H_2O and SO_3 when volatilized the volume of the vapor would be doubled and the density would be half the above figure. When the density of the vapor is actually determined, it is found to be 24.5, and this proves that the splitting up referred to must occur. We have already studied a similar case under ammonium chloride (p. 108).

Sulphuric acid and water dissolve each other in all proportions, and much heat is liberated when the two liquids are mixed. *The acid must always be poured in a thin stream into the water, never the reverse.* The acid has a violent action upon organic tissues, and must be removed at once, if got on the skin, by copious washing with water.

We have already noticed instances of the action of sulphuric acid upon the metals. Upon some, like iron and zinc, the dilute acid acts, liberating hydrogen. Upon others, like copper and mercury, the dilute acid has little or no action, but the hot strong acid attacks the metal energetically, liberating no hydrogen, but sulphur dioxide instead.

Most of the sulphates of the metals are soluble in water. We have seen that barium sulphate is insoluble, and that its formation is employed as a test both for $\overset{++}{Ba}$ ions and $\overset{--}{SO_4}$ ions.

Many other acids composed of hydrogen, sulphur, and oxygen are known. The only one we shall discuss is

341. **Thiosulphuric acid,** $H_2S_2O_3$. This name means sulpho-sulphuric acid, and the compound is so called because it may be regarded as sulphuric acid in which one oxygen atom has been replaced by a sulphur atom. The acid itself has never been obtained, but its salts are well known. They are called the *thiosulphates*.

Sodium thiosulphate, $Na_2S_2O_3$, is the most important. It is produced when a solution of sodium sulphite is boiled with sulphur:

$$Na_2SO_3 + S = Na_2S_2O_3.$$
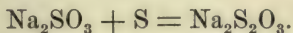
It forms large colorless crystals containing five molecular weights of water. It is very soluble in water, and the solution is largely employed in the fixing process in photography (p. 157), and also in the preparation of paper-pulp. The pulp is bleached by chlorine and the excess of chlorine must be removed, since it would injuriously affect the paper. Sodium thiosulphate accomplishes this. In this way it comes about that most finished paper contains a little sodium thiosulphate.

342. **Sulphur chloride,** S_2Cl_2, is produced when chlorine is led over melted sulphur heated in a retort. It is a heavy, yellow-brown liquid with a peculiar, unpleasant smell. It dissolves sulphur freely and is used in vulcanizing rubber, in which process the rubber takes up sulphur. Ordinary soft rubber contains 2 to 3 per cent of sulphur; hard rubber considerably more.

343. **Selenium** and **tellurium,** the remaining elements of the group, strongly resemble sulphur chemically, but are far less abundant. Their hydrogen compounds (H_2Se and H_2Te) are colorless, foul-smelling, highly poisonous gases. *Selenic acid,* H_2SeO_4, corresponding to H_2SO_4, is interesting because it is able to dissolve gold.

CHAPTER XXXVI

MANGANESE

Mn = 55.

344. This metal bears about the same relation to chlorine as chromium does to sulphur. It is a metal very similar to iron, and like chromium it enters into the structure of acids, which, like the corresponding chromium compounds, are known only as salts.

345. Occurrence.—*Manganese carbonate*, $MnCO_3$, and various oxides of the element occur in nature, but the most abundant and important compound is *manganese dioxide*, MnO_2. This occurs as the mineral *pyrolusite* in gray-black, metallic-looking crystals which yield a black powder. We have discussed the use of manganese dioxide for the preparation of chlorine (p. 73), and it is still much employed on the large scale for this purpose, but it is almost certain that the manufacture of chlorine by the electrolysis of sodium chloride solution will shortly displace this older method.[1]

Manganese is widely distributed. Traces are contained in sea-water, in most spring waters, and in many animals and plants.

Preparation.—Manganese is best obtained by heating strongly at one point a mixture of manganese dioxide and powdered aluminium. The reaction spreads through the mass, which is carried to an extremely high temperature by

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[1] Chlorine is now largely made, especially in Germany, by the electrolysis of a solution of potassium chloride, KCl.

the heat liberated in the chemical change. Aluminium oxide and manganese are produced:

$$3MnO_2 + 4Al = 2Al_2O_3 + 3Mn.$$
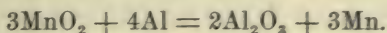
346. Properties.—Manganese is a reddish-gray metal with a strong luster. It is about as hard as iron and, when pure, is scarcely acted upon by the air. Even weak acids readily dissolve it, liberating hydrogen and producing *manganous* salts, in which the manganese is bivalent:

$$Mn + 2\overset{+}{H} = \overset{++}{Mn} + H_2, \text{ or}$$
$$Mn + 2HCl = MnCl_2 + H_2.$$
<center>Manganous
chloride.</center>
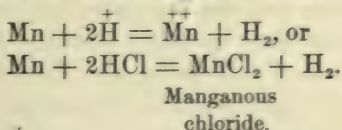
These salts are the most stable and important compounds in which manganese plays the *rôle* of a metal. The ion $\overset{++}{Mn}$ communicates a delicate rose-color to liquids containing it, and since this color is due solely to the manganese ion, the solutions of all manganous salts have the same color (p. 131). Crystallized manganous salts have the same tint.

Manganous sulphate, $MnSO_4$, is a white powder, soluble in water. When the solution is evaporated, crystals separate which may contain 1, 4, 5, or 7 H_2O, according to the temperature. As usual in such cases, the higher the temperature of crystallization the less water in the crystals (p. 175). The crystals are rose-colored, like the other manganous salts.

The oxide corresponding to these salts is, of course, the oxide in which manganese is bivalent—that is, *manganous oxide*, MnO. It is a green powder, made by heating the carbonate in the absence of air:

$$MnCO_3 = MnO + CO_2.$$

**347.** There is also an oxide Mn_2O_3, in which the metal is trivalent. It is a black powder. Corresponding to it is a series of un-

stable salts which also contain trivalent manganese—e. g., *manganic sulphate*, $Mn_2(SO_4)_3$. These are called the manganic salts. Their solutions contain the ion $\overset{+++}{Mn}$, and are colored violet.

Various other oxides of manganese are known. We shall only mention

348. *Manganese heptoxide*, Mn_2O_7, which is interesting because it corresponds to chlorine heptoxide, Cl_2O_7, and therefore forms one of the few points of resemblance between manganese and the halogens. It is a thick liquid with a greenish-black metallic luster. When carefully heated it passes into a purple vapor. It is a dangerous substance and often spontaneously separates into manganese dioxide and oxygen, with energetic explosion:

$$Mn_2O_7 = 2MnO_2 + 3O.$$
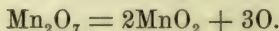
349. *Permanganic acid*, $HMnO_4$.—When manganese heptoxide is dissolved in much cold water, the liquid acquires a beautiful reddish-violet color, and is found, when the usual tests are applied to it, to contain an acid. A chemical reaction has occurred, and *permanganic acid*, $HMnO_4$, is dissolved in the water:

$$Mn_2O_7 + H_2O = 2HMnO_4.$$
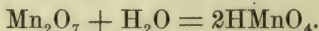
Permanganic acid is unstable, and is only known in solution, but its salts can readily be obtained. The most important salt is

Potassium permanganate, $KMnO_4$, which forms almost black crystals, with a greenish metallic luster. It is quite soluble in water, and the solution has the same magnificent red-violet tint which we have already noticed in the water solution of permanganic acid, and which, of course, is due to the ion $\overline{Mn}O_4$. It is clear from the formula that potassium permanganate is rich in oxygen. This oxygen is not firmly held and is easily given up to any oxidizable sub-

stance. Hence the solution of the salt is a powerful oxidizing agent and is much employed for that purpose. Thus it attacks and destroys most kinds of organic matter, producing very much the same effect in the cold as free oxygen at high temperatures.

CHAPTER XXXVII

THE HALOGENS

Fluorine, F.   Chlorine, Cl.   Bromine, Br.   Iodine, I.

350. These four elements, taken together, are called the halogens. They resemble each other strongly. In their compounds with hydrogen and the metals they are univalent. The hydrogen compounds (HF, HCl, HBr, and HI) are colorless, suffocating gases, very soluble in water, and their solutions are strongly acid. The compounds of these four elements with the same metal usually crystallize in the same form. Thus NaF, NaCl, NaBr, and NaI all crystallize in cubes. The intensity of the color of the elements increases from fluorine ($F = 19$), which is a gas of a somewhat paler color than that of chlorine, down to iodine ($I = 127$), which is almost opaque, but in a thin film allows a little reddish-brown light to pass. In the same order the chemical activity and non-metallic character decrease. Fluorine is the most energetic non-metal, and by far the most active, chemically, of all the elements, and the tendency of the halogens to enter chemical changes decreases down to iodine, which, however, is by no means inert.

Chlorine, which has already been described (p. 76), is the most abundant, and fluorine comes next. Bromine and iodine are far less common. These elements only occur in compounds in nature; never native.

FLUORINE, F = 19.

351. Occurrence.—The chief natural fluorine compound is fluorspar, calcium fluoride, CaF_2, an abundant and important mineral. It crystallizes in cubes which are colorless and transparent when pure, but usually colored by impurities. Some samples of it contain, in addition to the fluorine combined with the calcium, *free fluorine* dissolved in the crystals of calcium fluoride. It escapes as gas when the crystals are powdered. Fluorine, therefore, occurs in the free state in nature, but only in traces. Compounds of fluorine are widely distributed. They are found in traces in river and sea water, in many plants, and in the bones, teeth, blood, and brain of animals.

352. Preparation.— Fluorine is made by the electrolysis of liquid anhydrous hydrofluoric acid, HF. Since hydrofluoric acid itself is almost a nonconductor of the current, some potassium hydrogen fluoride, KHF_2, is dis-

FIG. 48.—Isolation of fluorine.

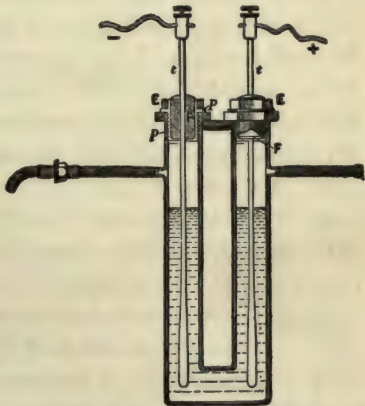solved in it. It then conducts fairly well. This liquid is placed in a ∪-shaped tube of copper (Fig. 48). This tube is closed by stoppers, *F F,* made of fluorspar, through which pass the platinum electrodes, *t t,* which convey the current. Through side tubes the gaseous products of the electrolysis escape and can be examined. The copper tube is immersed in a freezing mixture, for the electrolysis must be carried out at a low temperature to prevent the vaporization of the hydrofluoric acid. Equal volumes of hydrogen and

fluorine are produced. The hydrogen is liberated from the negative pole and the fluorine at the positive.

353. **Properties.**—Fluorine is a gas of a color somewhat similar to that of chlorine, but paler. Its odor is distinct from that of chlorine, but it has the same irritating action upon the mucous membranes. When the gas is passed into a vessel cooled by being surrounded by liquid air it condenses to a yellow liquid which is slightly heavier than water.

The chemical activity of fluorine is extraordinary, and in this respect it easily stands first among the elements. All of the metals—even gold and platinum—are attacked by it and converted into fluorides. In the case of copper the action is slight, and for this reason copper is employed in the construction of the apparatus used in the preparation of the element. Sulphur, phosphorus, and most of the other non-metals ignite spontaneously in the gas, and burn to the corresponding fluorides. Even bromine and iodine, which are very similar to fluorine chemically, take fire in it and burn energetically, and this fact is worth noting, for, as a rule, elements which closely resemble each other in their chemical conduct show little tendency to unite. Fluorine appears to have no action upon chlorine nor upon oxygen. When a tube from which fluorine is escaping is brought into an atmosphere of hydrogen there is an explosion, and the fluorine burns to hydrofluoric acid, HF, producing a hot blue flame. This occurs in the dark as well as in daylight. (Compare the behavior of chlorine and hydrogen, p. 78.)

Fluorine also acts violently upon many compounds. When it is passed into a test-tube containing a little dry salt (NaCl) at the bottom, the tube at once becomes full of chlorine, sodium fluoride being produced:

$$NaCl + F = NaF + Cl.$$
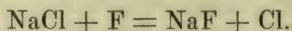
In the same way it acts upon other chlorides. Its action upon iodides is similar, but the iodine, which is liberated

at first, burns afterward to iodine fluoride. It reacts with water instantly, even in the dark (compare the same reaction with chlorine, p. 79), forming hydrofluoric acid and liberating oxygen as *ozone*. Its action upon other hydrogen compounds is similar. Thus, when liquid fluorine is spilled upon the floor, a flame rises which is due to the combination of the fluorine with the hydrogen of the wood. Fluorine does not act upon glass, and, if it is *perfectly* pure, it can be preserved sealed up in glass tubes.

354. **Hydrofluoric acid,** HF, is produced with explosion, when hydrogen and fluorine are brought together. It is made by the action of strong sulphuric acid on powdered calcium fluoride at a gentle heat:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
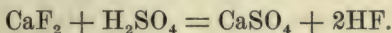
Since the acid acts rapidly upon glass, this operation must be conducted in vessels of platinum or of lead. If a water solution of the acid is required, the mixture of calcium fluoride and sulphuric acid is heated in a lead retort, and the gaseous HF brought into contact with water contained in a platinum dish. If, on the other hand, it is desired to obtain the acid free from water, the gas is led into a platinum bottle surrounded by a freezing mixture. Hydrofluoric acid is thus obtained as a colorless liquid, which must be kept in a freezing mixture, since otherwise it will vaporize and burst the bottle, if the latter is sealed.

Hydrofluoric acid is a colorless, poisonous gas, with a suffocating odor. It is freely soluble in water to a colorless fuming liquid, which is strongly acid and readily dissolves zinc, iron, silver, and many other metals, liberating hydrogen and forming the corresponding fluorides. Commercial hydrofluoric acid is the water solution of the gas. On account of its action upon glass it is sold in bottles of hard paraffin, upon which it has no action.

Over a little finely powdered silica, SiO_2, contained in a

platinum crucible we pour carefully some strong hydro-
fluoric acid. There is a violent reaction, heat is produced,
the white powder disappears, and a colorless suffocating
gas escapes, which produces fumes in the air. This gas is
silicon fluoride, SiF_4, produced thus:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$
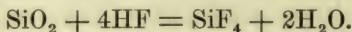
This experiment will help us to understand the action
of hydrofluoric acid on glass.[1] For etching on glass, gaseous
HF is usually employed. In marking the graduations on a
thermometer tube, for instance, the tube is first coated thin-
ly with wax and then the divisions scratched through the
coating, laying bare the glass. In this condition the tube
is exposed for a time to hydrofluoric acid gas, produced by
a mixture of calcium fluoride and strong sulphuric acid.
When the wax is removed the divisions are found etched on
the glass.

The water solution of hydrofluoric acid acts violently
upon the skin, and care must be taken not to get it upon
the hands. Its vapor is poisonous and must not be inhaled.

Chlorine has already been described (Chapter X).

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[1] Read again the paragraphs on the composition of glass (p. 199).

	At. Wt.	Melt	Boil	
F	19	−223°	−187°	pale yellow gas
Cl	35,5	−102°	−33,6°	greenish yellow gas
Br	80,	−7°	59°	red liquid
I	127	107°	175°	purplish black

CHAPTER XXXVIII

BROMINE AND IODINE

Bromine, Br = 80.

355. Some potassium bromide, KBr, is dissolved in water and a little chlorine gas passed into the liquid. At once the red color of bromine appears in the solution and, if much potassium bromide was used and the current of chlorine be continued, drops of bromine will collect under the solution. The solution of potassium bromide contains bromine ions $\overset{-}{\text{Br}}$, and the tendency of chlorine to exist as an ion is greater than that of bromine, so that the reaction

$$2\overset{-}{\text{Br}} + \text{Cl}_2 = 2\overset{-}{\text{Cl}} + \text{Br}_2$$
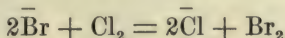
occurs, and bromine separates.

356. **Occurrence and preparation.**—The occurrence of great deposits containing potassium chloride at Stassfurt, in Germany, has been mentioned. This potassium chloride is separated from other substances which occur along with it by treating the deposit with water and then crystallizing the potassium chloride from the solution. Now the liquid from which the potassium chloride has separated contains bromine ions, and when treated with chlorine, as in the experiment just described, bromine is obtained. The liquid is hot when the chlorine is introduced, and the bromine escapes as a vapor, which is condensed. About two-thirds of the bromine of the world is made at Stassfurt. The rest is extracted by similar methods from the waters of

salt springs in the United States. The water of the Dead Sea contains bromine ions, and is likely to be employed for the production of the element in the near future.

357. Properties.—Bromine is a black-red, almost opaque liquid, about three times as dense as water. When slightly cooled it solidifies to a mass somewhat resembling iodine. At ordinary temperatures, and more rapidly when heated, the liquid gives off red bromine vapor, the odor of which recalls that of chlorine. Its action upon the eyes, nose, and throat is even more violent than that of chlorine. The density of bromine vapor is about 80 referred to hydrogen, and this shows that the molecular weight is about 160. Hence the formula is Br_2—the bromine molecule contains two atoms. This is also the case with the other halogens.

Bromine is an energetic element. It unites directly with nearly all of the metals, forming the corresponding bromides. Sometimes the combination is violent. A small fragment of potassium dropped into bromine produces a loud explosion. Curiously enough, it is quite without action on sodium, which is so similar to potassium. When a hydrogen flame is lowered into bromine vapor it continues to burn, producing colorless, suffocating hydrobromic acid, HBr. Bromine and oxygen have no action upon each other, and no compound of the two elements has ever been obtained. Bromine is soluble in water, and the red solution produced is called bromine water and is used in the laboratory. Of course this solution does not contain bromine ions. It contains bromine as Br_2. Bromine ions can only exist in presence of an equivalent number of positive ions, like those of $\overset{+}{K}$ or $\overset{+}{Na}$. When bromine water is placed in sunlight, the following reaction slowly takes place:

$$Br_2 + H_2O = 2HBr + O,$$
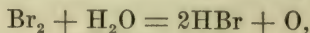
and oxygen collects in the vessel.

Bromine is a splendid disinfectant, and is employed for

this purpose, but not largely, because it is too expensive. The most important compound of bromine is

358. **Potassium bromide**, KBr, which crystallizes in colorless cubes which have a pleasant saline taste and are freely soluble in water. It is largely employed in medicine in diseases of the nervous system, and also in photography. When added to the *developer* (p. 156) it prevents the production of an image upon those parts of the plate which have only slightly been affected by light. It is employed therefore in developing plates which have accidentally been exposed too long in the camera.

359. *Hydrobromic acid*, HBr, corresponds to hydrochloric acid. It results when dilute sulphuric acid acts upon the bromide of a metal—on KBr, for instance.[1] The equation is

$$2KBr + H_2SO_4 = K_2SO_4 + 2HBr.$$
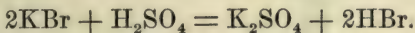
Another method of making hydrobromic acid is to pass a mixture of hydrogen and bromine vapor over red-hot platinum. This mixture is easily obtained by passing hydrogen through liquid bromine. The bottle containing the bromine is placed in warm water, which causes the bromine to vaporize abundantly. The hydrogen charged with bromine vapor

Fig. 49.—Union of hydrogen and bromine to hydrobromic acid.

passes into a wide glass tube, which contains a spiral of platinum wire kept at a red heat by the passage of an electric current. Here the combination takes place, and the

[1] This method of making HBr is excellent and has the advantage of perfect analogy to the preparation of hydrochloric acid by the action of sulphuric acid on salt. The usual statement that it is impossible to obtain HBr by a similar reaction is quite without foundation.

hydrobromic acid can be passed into water and a solution of it obtained.[1] The arrangement of the apparatus is shown in Fig. 49.

Hydrobromic acid is similar to hydrochloric acid. It is a colorless, suffocating gas, which produces fumes in the air and has a pungent, irritating odor. It is excessively soluble in water, and the solution is strongly acid, for a very large proportion of the dissolved HBr is dissociated into $\overset{+}{H}$ and $\overset{-}{Br}$ ions.

<div align="center">IODINE, I = 127.</div>

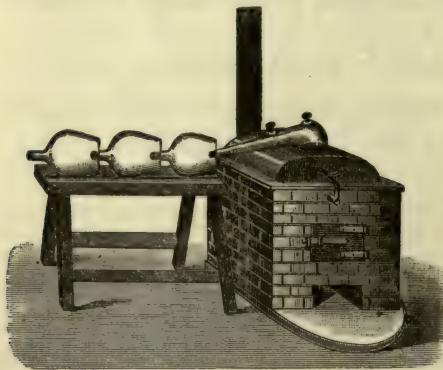**360. Occurrence and preparation.**—Traces of iodine compounds are contained in sea-water, and larger quantities in sea-weeds, especially in those which grow at great depths. The manufacture of iodine from sea-weeds is carried on in Scotland and France. The weeds are first burned, and by systematically treating the ashes with water a liquid is finally obtained which contains the iodides.

FIG. 50.—Extraction of iodine.

This is mixed with manganese dioxide and sulphuric acid and distilled. The vapor of iodine is liberated and is condensed in pear-shaped clay receivers:

$$2NaI + MnO_2 + 3H_2SO_4 =$$
$$2NaHSO_4 + MnSO_4 + 2H_2O + I_2.$$

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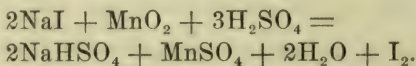
[1] This experiment is due to Newth, Chemical Lecture Experiments, p. 104.

The apparatus used is shown in Fig. 50. The iodine is purified by distillation.

Small quantities of potassium iodate, KIO_3, corresponding to potassium chlorate, $KClO_3$, are contained in the sodium nitrate deposits of Chili (p. 116). The preparation of iodine from this source has become of great importance and threatens soon to displace altogether the production of iodine from sea-weed.

361. **Properties.**—Iodine crystallizes in shining gray-black plates, which have the color and luster of graphite. It melts to a thick black liquid slightly above the boiling-point of water and boils at a higher temperature. When mixed with air the vapor of iodine has a magnificent violet color, but the pure vapor is deep blue. Its density shows that the formula is I_2. It is probable that all substances which vaporize at all, do so at all temperatures, but at high temperatures the vaporization is rapid, and therefore noticeable. Iodine is a good example of this. If a little iodine is placed in a bottle and the stopper inserted, the space above the solid will soon be colored distinctly violet by the vapor, and, after a time, small glittering crystals of iodine will condense upon the glass in the upper portion.

Iodine is only very slightly soluble in water, but it dissolves freely in alcohol, ether, chloroform, and carbon disulphide. The alcoholic and ethereal solutions are reddish-brown, while the solutions in chloroform and carbon disulphide have a violet tint resembling that of iodine vapor.

Iodine is less active chemically than the other halogens, but still quite energetic. It unites with most of the metals, especially when heated, and in some cases—with potassium, for instance—the combination takes place with violent energy. With hydrogen it only unites at a high temperature, and then only partially.

362. *Hydriodic acid*, HI, is a colorless, fuming, suffocating gas which dissolves very freely in water to a strongly

18

acid liquid. It resembles HCl closely, but is much more readily decomposed by heat.

363. **Potassium iodide**, KI, is the most important salt of hydriodic acid, and, in fact, the most important iodine compound technically. It forms colorless cubical crystals which dissolve readily in water. It is much employed in medicine.

364. Only one compound of iodine and oxygen is known with certainty. This is

Iodine pentoxide, I_2O_5, a white powder which is made by gently heating *iodic acid*, HIO_3 (analogous to $HClO_3$). It dissolves in water, and the solution is found to contain iodic acid—

$$I_2O_5 + H_2O = 2HIO_3.$$
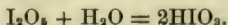
Iodine pentoxide is easily separated into iodine and oxygen by heat.

Many salts are known in which the hydrogen of iodic acid is replaced by metals. These are called iodates. Potassium iodate, KIO_3, has been mentioned (p. 259).

365. Free iodine produces an intense blue color with starch paste. The nature of the blue substance still remains unknown. The test is extremely delicate. We have seen that the mixture of starch paste with an iodide, like KI, can be used as a test for ozone, or, in fact, for anything which will set free the iodine (p. 45).

366. **General remarks.**—The halogens form one of the best examples of a natural family or group of elements. The sodium group (p. 135) is another remarkable instance of the natural relationship of a number of elements. The student should compare these two groups with each other. He will find that in each group the resemblance of any element to the other elements of the same group is striking. On the other hand, the comparison of sodium with fluorine, or of potassium with chlorine, will give him a vivid and accurate idea of the nature of the differences between metals and non-metals—that is, between positive and negative elements.

CHAPTER XXXIX

IRON
Fe = 56.

367. Iron is very similar to *manganese*, which precedes it in the order of increasing atomic weights (Mn = 55). On the other hand, it has many points of resemblance with *nickel* and *cobalt*, which follow it (Ni = 58.7, Co = 59). Iron and nickel occur together in meteorites, and cobalt and nickel are always associated in nature. All three metals are strongly attracted by the magnet. Iron is by far the most abundant and important.

368. **Occurrence.**—Iron was employed for weapons and other cutting implements by prehistoric man. The native metal is rare (except in meteorites), but iron compounds are so common that the metal stands fourth in order of abundance. The oxides and hydroxides of iron are its most important ores. Iron disulphide, FeS_2, is the very common mineral *pyrite*. Various other iron compounds enter largely into the structure of rocks. It is safe to assume that whenever a rock or a soil is colored red, yellow, or green, the color is due to iron in some form. Rocks are often colored red by ferric oxide, Fe_2O_3, yellow by ferric hydroxide, $Fe(OH)_3$, and green by various silicates of iron. Iron is only contained in small quantities in the bodies of animals and plants, but nevertheless it plays an important *rôle*. In both it is connected with the process of respiration. The green parts of plants, in which the carbon dioxide of the air is decomposed, the carbon built into the structure of the

plant and the oxygen returned to the atmosphere, contain iron, and it has been shown that if no iron compounds are supplied to the plant the green substance is no longer formed and respiration ceases. In animals the iron is contained in the red blood-corpuscles, by means of which oxygen is taken from the air.

369. Preparation and properties.—Pure iron can be obtained by heating pure ferric oxide in hydrogen:

$$Fe_2O_3 + 3H_2 = 3H_2O + 2Fe.$$
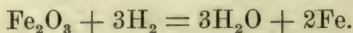
Pure iron, in a compact mass, has a silver-white metallic luster which is permanent in dry air, but rapidly lost under the action of air and water together. At the same time a yellow-brown coating called "rust" appears on the iron. This contains ferric hydroxide and ferric oxide, and has the following composition:

$$Fe_2O_32Fe(OH)_3.$$
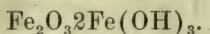
When rusting has once begun it proceeds more and more rapidly until the change is complete.

When pure, iron melts only at 1800°, which is very much above a white heat (about 1200°). At the temperature of the electric arc it boils, rapidly disappearing as vapor. When heated to redness in the air, the surface of the metal is converted into an oxide, and iron will burn brilliantly in oxygen at high temperatures. Very finely powdered iron takes fire spontaneously in the air. Iron dissolves easily in acids.

370. Preparation of iron on the large scale.—This is the object of the BLAST-FURNACE PROCESS. The principle of the process is simple and is one that we have repeatedly met. At high temperatures carbon acts on iron oxide as it does on other metallic oxides, converting it into metal. The blast furnace may be 100 feet high, and its interior is egg-shaped, so that the widest part—which may be 25 feet

ROBERT WILHELM BUNSEN
B. Germany, 1811. D. 1899.

across—is much nearer the bottom than the top. At the top the ore is introduced, together with some form of carbon, often coke. At the bottom the liquid iron collects and is allowed to flow out at intervals and received in a bed of sand, which is arranged beforehand in such a way that the iron flows into small hollows provided for it, and solidifies there to *pig-iron*. A blast of hot air under some pressure is introduced near the bottom of the furnace, and the burning of the carbon by the oxygen supplied in this way keeps the temperature of this portion at a bright-yellow heat. The upper portions are not so hot.

This is an outline of the process as it might be worked with pure iron oxide to produce a pure iron. Now come some complications. No actual iron ore is pure Fe_2O_3. All ores contain a variety of impurities, of which the most important to us at present are silica, SiO_2, and aluminium oxide, Al_2O_3. Along with the coke and ore, limestone is added at the top of the furnace. The lime of the limestone and the silica and Al_2O_3 of the ore unite to produce a silicate of calcium and aluminium, which melts readily and collects as a liquid mass over the melted iron. This is called the slag. It is allowed to run out by an orifice called the slag-hole, which is at a higher level than the hole through which the melted iron is tapped. The iron obtained in this way is never pure. It contains from 2 per cent upward of carbon, some silicon, and smaller quantities of phosphorus, sulphur, and other substances. It is called pig-iron or cast iron.

Wrought iron, or malleable iron, is far purer than pig-iron. It is made from pig-iron by the *puddling process*. This consists in heating the pig-iron to a high temperature in contact with ferric oxide, Fe_2O_3, and in an atmosphere containing abundant oxygen from the air. Partly by the oxygen of the ferric oxide and partly by that of the surrounding atmosphere the carbon is burned to CO, carbon

monoxide, which escapes as gas, and the silicon to SiO_2, which goes into the slag. At the same time the phosphorus, sulphur, and other impurities are also removed by oxidation. Wrought iron is softer and more tenacious than cast iron, and melts at a higher temperature. Before it melts it softens and becomes somewhat plastic, and this is a most important property, for it makes it possible to hammer a piece of iron into any desired shape or to weld two pieces together.

371. **Steel** contains more carbon than wrought iron, but less than cast iron. The finest steel—called crucible steel— is made by heating bars of wrought iron for a week or more in contact with powdered charcoal. The iron slowly takes up carbon, and each bar—even in the interior—is converted into steel. The bars are afterward melted in crucibles in order to secure uniformity in the product. Such steel is used for the finer grades of cutlery.

Steel is harder and even more tenacious than wrought iron, and melts at a lower temperature. Another important difference is the fact that steel can be tempered, which is not the case with iron, either wrought or cast. The cheaper varieties of steel—rail steel, bridge steel, and so on—are made in enormous quantities by other processes which can not be discussed here. They are described completely in works on metallurgy. Some idea of the importance of iron and steel in modern life may be gained from the fact that in 1903 nearly 18,000,000 tons of pig-iron were produced in the United States alone. This corresponds to over 500 pounds for every inhabitant of the country.

372. *Ferrous oxide,* FeO, is a black powder which easily takes up oxygen in the air, passing into ferric oxide. *Ferrous hydroxide,* $Fe(OH)_2$, is white, and, when exposed to air, turns first green and then red-brown, being converted into ferric hydroxide, $Fe(OH)_3$. Both ferrous oxide and ferrous hydroxide dissolve in acids yielding the ferrous

salts in which iron is bivalent. The formulas of the ferrous correspond therefore to those of the corresponding compounds of magnesium or zinc. For example:

> Ferrous chloride, $FeCl_2$.
> Ferrous bromide, $FeBr_2$.
> Ferrous nitrate, $Fe(NO_3)_2$.
> Ferrous sulphate, $FeSO_4$.

Ferrous salts are produced when iron dissolves in acids; thus:

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$
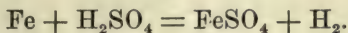
They are green when crystallized and pale green or colorless when dissolved in water. The most important ferrous salt is

373. **Ferrous sulphate,** $FeSO_4$, which can be obtained, as indicated above, by the action of dilute sulphuric acid on iron. It can be more cheaply made at present by the spontaneous oxidation of ferrous sulphide, FeS, under the influence of air and water. It forms green crystals with $7H_2O$, which have long been known as " green vitriol " or " copperas." It is an excellent disinfectant.

All the ferrous salts absorb oxygen and pass into ferric salts when preserved. For this reason they must be kept in well-closed bottles.

374. *Ferrous sulphide,* FeS, is produced as a black precipitate when ferrous ions, $\overset{++}{Fe}$, and sulphur ions, $\overset{--}{S}$, are brought into the same solution, i. e., when a solution of a ferrous salt is mixed with one of a soluble sulphide—

$$FeCl_2 + Na_2S = 2NaCl + FeS.$$
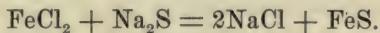
The iridescent film which forms over the surface of stagnant water in pools and ditches consists of ferrous sulphide. It is readily obtained as a grayish-black, dense, metallic, fused mass by melting iron and sulphur together. It is

employed in the laboratory in the production of **hydrogen sulphide** (p. 237).

375. Ferric oxide, Fe_2O_3, occurs in nature as the mineral *hæmatite* in steel-gray crystals, which leave a red streak when drawn over an unglazed porcelain plate, and yield a red powder when pulverized in a mortar.

Ferric hydroxide, $Fe(OH)_3$, is precipitated in rust-colored flakes when a solution of a hydroxide is added to one containing a ferric salt—
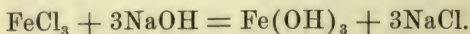
$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl.$$
Ferric chloride.

Colloidal solutions.—Besides the ordinary insoluble ferric hydroxide there is another modification of it which, when treated with water, apparently dissolves, forming a clear dark-red liquid, which leaves no residue when passed through a filter. We have seen that ordinary solutions—like that of common salt in water boil at a higher and freeze at a lower temperature than water alone. But this solution of ferric hydroxide boils at 100° and freezes at 0°, just as though the water was free from dissolved substance. This looks as though the ferric hydroxide was not really dissolved in the water, but only suspended in particles too fine to be detained by a filter, and this idea is strongly supported by the fact that when a beam of electric light is passed through the liquid in a dark room, the track of the beam is distinctly visible, which is not the case with true solutions. This indicates the presence of minute solid particles which reflect the light to the eye and make it visible, just as the path of a sunbeam is visible in dusty air. Many other substances ordinarily insoluble in water have been obtained in a similar condition. Among these are sulphur and many of the metals—for instance, platinum, silver, and gold. This curious state of things is called *colloidal solution*, and, for the reasons just stated, it is regarded at present as nothing but suspension, in which the solid particles are very small. The colloidal solutions of the metals are clear, deep brownish liquids from which, when they are preserved, the metal gradually settles as a powder.

376. *Ferric salts.*—Ferric oxide dissolves with difficulty and ferric hydroxide with ease in acids, both producing

ferric salts, in which the iron is trivalent. Ferric salts which contain water of crystallization are brownish-yellow in the solid state, and their solutions have the same color.

Ferric chloride, $FeCl_3$, has been found in the craters of volcanoes. It is made by burning piano-wire (the purest commercial form of iron) in a rapid current of dry chlorine. It forms iron-black, glittering, tabular crystals, which are very soluble in water. When the solution is evaporated, and then allowed to crystallize at ordinary temperatures, the hydrate $FeCl_3 6H_2O$ separates in brownish-yellow crystals. This is the ordinary ferric chloride of commerce. Several other hydrates are known.

The oxide Fe_3O_4 occurs in nature in black crystals which are attracted by the magnet. Some specimens are naturally magnetic, and to these the name *lodestone* is given. Fe_3O_4 is called *magnetic iron oxide* or *magnetite,* and is an important iron ore.

It is doubtful whether any salts corresponding to this oxide exist. The chloride would, of course, be Fe_3Cl_8, and it has been described, but it is very likely only a mixture of ferric and ferrous chlorides, thus : $FeCl_2 2FeCl_3$.

377. **Iron disulphide,** FeS_2, is the very common mineral pyrite. It is brass-yellow, with a metallic luster, and the crystals are often cubical. It is too hard to be scratched with a knife, and hard enough to yield sparks when sharply struck with a piece of steel. Great quantities of pyrite are burned for the production of sulphuric acid (p. 242). It is of no value as an iron ore, for some of the sulphur would find its way into the iron and reduce its tenacity to such an extent as to render it worthless.

CHAPTER XL

COBALT AND NICKEL—THE PLATINUM METALS

378. *Cobalt* and *nickel* resemble iron, and are remarkably similar to each other. They are both hard, white metals with a somewhat gray luster, which melt only at a high white heat. They are unaffected by the air at ordinary temperatures, but at a red heat each becomes covered with a scaly coating of the corresponding oxide. Like iron, they are attracted by the magnet. They are only slowly acted upon by hydrochloric and sulphuric acids, but dissolve readily in nitric acid. Chemically, they differ from iron chiefly in this respect, that cobalt and nickel each form only one series of stable salts—those in which the metal is bivalent. These salts correspond to the ferrous compounds. Simple salts corresponding to the ferric compounds are unknown with both nickel and cobalt, though the oxides Co_2O_3 and Ni_2O_3 have been obtained. Native nickel and cobalt are found only in meteorites, which consist, for the most part, of iron alloyed with rather large quantities of nickel and with traces of cobalt and other elements. Cobalt and nickel compounds are generally found together in nature. The chief ores are the compounds of the metals with sulphur and arsenic.

379. *Cobaltous oxide*, CoO, is a brown powder. This oxide corresponds to the cobalt salts—$CoCl_2, Co(NO_3)_2$, $CoSO_4$, and so on. These salts are blue when free from water, but when they contain water of crystallization they are red, and their water solutions are rose-red. Since

268

cobalt nitrate, cobalt chloride, and the other cobalt salts all have just the same color when dissolved in water, this must be the color of the cobalt ion, $\overset{++}{Co}$. On the other hand, anhydrous cobalt chloride is deep blue, and, when dissolved in alcohol, yields a blue solution which does *not* conduct the current. The blue color must be due, therefore, to the undissociated molecules $CoCl_2$. Owing to this difference in color, a water solution of cobalt chloride forms a kind of *sympathetic ink*. The color of the cobalt ion is not very intense, and writing made with the dilute solution on paper is invisible and remains invisible when the excess of water evaporates. But when the paper is warmed, the strongly colored anhydrous salt is produced and the writing appears in blue characters, which again disappear, after a time, on cooling, because the $CoCl_2$ absorbs water from the air.

380. *Uses.*—Cobalt as metal has found no commercial applications. Cobaltous oxide, when added to melted glass, dissolves in it as cobalt silicate, producing an intensely blue mass, which, when cooled and powdered, constitutes the blue color called *smalt*.

381. *Nickelous oxide,* NiO, which is the oxide corresponding to the nickel salts, is green. Anhydrous nickel salts are yellow, those containing water of crystallization green. Dilute water solutions of all nickel salts have the same emerald-green color, which is that of the nickel ion $\overset{++}{Ni}$.

382. **Uses of Nickel.**—On account of its luster and permanence in the air, nickel is largely used for plating articles made of iron and other metals. This is effected by hanging the object in a water solution of a nickel salt, and making it the negative pole of a current passing through the liquid. The positive pole is a bar of pure nickel, which dissolves as nickel deposits at the negative pole, and keeps the number of nickel ions in the liquid the same. *German silver* is an alloy of nickel with copper and zinc. The nickel

coins of the United States, Germany, and Belgium contain 25 per cent of nickel and 75 per cent of copper.

THE PLATINUM METALS

| Ruthenium, Ru. | Rhodium, Rh. | Palladium, Pd. |
| Osmium, Os. | Iridium, Ir. | Platinum, Pt. |

383. A reference to the table of atomic weights will show that the first three of these metals, Ru, Rh, and Pd, have atomic weights in the neighborhood of 100, while the atomic weights of the last three lie in the neighborhood of 200. Here we meet with a confirmation of a statement which has been made before—that substances with high atomic weights have high densities also, for the densities of the first three are not far from 12, while those of Os, Ir, and Pt are above 20. *Osmium*, whose density is nearly 22.5, is the heaviest of all substances. *Palladium* dissolves in nitric acid. With this exception, the platinum metals are unaffected by the three ordinary acids singly. Aqua regia dissolves most of them, but some, like iridium, are scarcely affected by it. They are all white metals, with a strong grayish metallic luster, which is permanent in the air. They melt only at high temperatures, palladium having the lowest melting-point, while osmium has the highest. They are rather inert chemically, and their compounds are easily decomposed by heat, leaving a residue of the metal. They occur together in nature in rounded grains mixed with sand, in the same way as the placer deposits of gold.

384. Platinum is by far the most important metal of the group. It is a white metal, with a somewhat grayish tint, capable of taking a high polish, and very malleable and ductile. It melts only at 2000°—a temperature much beyond a white heat—but can be melted in the oxyhydrogen flame, and rapidly vaporizes when subjected to the heat of the electric arc. Finely divided platinum is black and is called *platinum black*. In this form the metal best exhibits its remarkable power of absorbing gases—a power which is shared by other metals of the group, especially by palladium. Platinum black will absorb 1,000 times its volume of oxygen or 300 times its volume of hydrogen. This phenomenon has

engaged the attention of chemists for a century, but we are still in doubt as to what happens. Either the gases dissolve in the metal, producing solid solutions, or else chemical combination occurs and unstable oxides and hydrogen compounds of platinum are obtained. An important practical point is, that when platinum black is exposed to a mixture of hydrogen and oxygen, both gases are absorbed, and, in contact the platinum, combine to form water so rapidly that the metal becomes red-hot and ignites the mixture. This is the principle of the self-lighting Welsbach mantles for gas-burners. Illuminating gas contains something like half its volume of hydrogen. Of course the oxygen comes from the air.

Owing to its high melting-point and its resistance to the action of most chemicals, platinum is much used for the construction of dishes and crucibles which are indispensable in the chemical laboratory. Platinum is not acted upon by any single acid, but is slowly dissolved by aqua regia. However, there are many substances which do act upon it, and which must not be heated in platinum vessels.

385. Platinum is either bivalent or quadrivalent in most of its compounds.

Platinum monoxide, PtO, is a gray, and *Platinum dioxide*, PtO$_2$, a black powder. Both are decomposed into platinum and oxygen by gentle heating.

Platinum dichloride, PtCl$_2$, is a greenish powder insoluble in water.

Platinum tetrachloride, PtCl$_4$, is yellow. It is produced when the metal is heated in a current of chlorine. It is readily soluble in water, and, when the liquid is evaporated, there separate red crystals of the composition PtCl$_4$5H$_2$O.

Both chlorides of platinum separate into metal and chlorine when strongly heated.

CHAPTER XLI

CARBON

C = 12.

386. For two reasons carbon is the most interesting of
all the elements. In the first place, the bodies of living
things, both animal and vegetable, are composed of carbon
compounds, and the study of these compounds has already
thrown much light, and will throw much more, upon the
nature of the chemical processes which are associated with
life. In the second place, the compounds containing carbon
are marvellously numerous, far more numerous than those
of all the other elements put together. We shall understand
clearly the reason for this as we proceed, and shall perceive,
at the same time, that the number of possible compounds
is infinite.

Carbon exists in several different modifications: First,
amorphous carbon, of which *coal* (*anthracite*), *charcoal*,
and *lampblack* are more or less impure varieties. Second,
crystalline carbon, which includes two very different sub-
stances, *graphite* and the *diamond*.

387. **Coal.**—In the geological history of the earth there
was one epoch, called the Carboniferous period, in which
vegetation was far more luxuriant than it is at present,
partly because the temperature was higher, partly because
the air was richer in carbon dioxide. Over vast marshy

plains, not far above sea-level, grew forests of whose rich-
ness and density a tropical jungle of the present day gives
only a faint idea. Leaves, branches, and trunks accumu-
lated where they fell, and in this way immense masses of
vegetable *débris* were produced, which were covered with
earth and converted into coal by a slow change in which the
pressure of overlying strata played an important part.
Vegetable matter—wood, for instance—contains mostly car-
bon, hydrogen, and oxygen, and the change into coal consists
in the removal of the last two elements with a portion of the
carbon, the rest of the carbon being left with all the mineral
matter of the original plant, as coal. This process is very
gradual, and all stages of it are found in nature. Here are
some examples:

1. *Peat* is plant-substance only slightly carbonized, and
still retaining a perfectly distinct vegetable structure.

2. *Lignite* is a brown, imperfect, woody coal found in
the newer rocks.

3. *Bituminous coal* still contains much hydrogen and
some oxygen. When it is heated gaseous compounds of
hydrogen and carbon escape, which burn with a bright flame,
while in the vessel there remains a grayish-black residue,
called *coke*, composed of carbon with some mineral matter.
Illuminating gas is made by heating bituminous coal in
fire-clay retorts and collecting the gas given off, after purify-
ing it, in gasometers.

4. *Anthracite coal* has lost almost all of its hydrogen,
and consists essentially of carbon with some mineral matter,
which remains as ash when the coal is burned. When
heated in the absence of air anthracite is almost unaltered
and little gas escapes.

388. **Charcoal** results when wood is heated in the absence
of air. This is best done in iron retorts, so that the valuable
products which vaporize can be condensed and collected.
The properties of charcoal depend on the temperature at

which it is prepared. When made at a low temperature it is brownish, and so inflammable that, if finely divided, it catches fire on contact with air. Charcoal made at a high temperature is grayish-black, denser, and not nearly so inflammable.

389. **Lampblack**, or **soot**, is a soft black powder which is produced when combustible substances rich in carbon, like turpentine or rosin, are burned in an insufficient supply of air. It is employed in the production of printer's ink. Its formation can be illustrated by placing a cold porcelain plate in an ordinary luminous gas flame, when a coating of lampblack is immediately deposited.

Crystalline Carbon

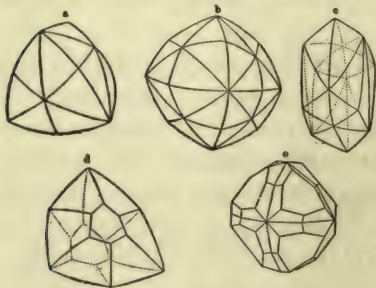390. **Graphite** occurs abundantly, especially in the older rocks. It is soft and gray, with a metallic luster. When drawn across paper it leaves a black mark. A mixture of graphite and clay is employed for the "lead" of pencils and for the manufacture of crucibles, to be employed in the melting of steel and in other processes requiring very high temperatures. *When any other modification of carbon is heated to extremely high temperatures it is transformed into graphite.* Thus, when a diamond is introduced into the electric arc it swells up and a mass of graphite is produced. When a crucible made of charcoal is heated in the electric furnace to a temperature of 3,000° or over it is completely converted into graphite in a few minutes. From facts of this kind we know that, at high temperatures, graphite is the stable modification

Fig. 51.—Diamond crystals.

of carbon. Of course one of the modifications must be the natural state at ordinary temperatures, and the others must be slowly passing into it, just as colorless phosphorus slowly passes into the red variety. But it is impossible to say which modification of carbon is the stable form at ordinary temperatures, for the speed with which the others change into this form (whichever it may be) is so small that all the modifications appear to be permanent.

Fig. 52.—Artificial diamonds.

391. **Diamond** occurs native in certain localities, particularly in Brazil and at the Cape of Good Hope. It differs from the other forms of the element in its high density (3.5), its great hardness, and its high index of refraction. It exceeds all minerals in hardness, and one form of it called carbonado, which is black and not well crystallized, is the hardest of all substances. The diamond may be colorless, yellow, brown, or black, according to its purity.
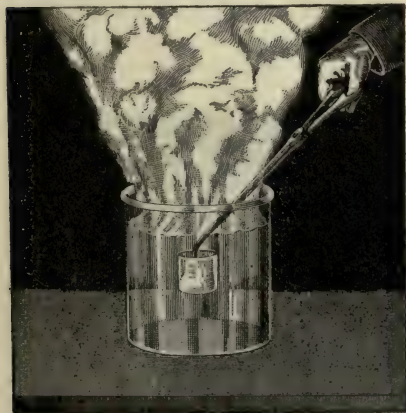
Fig. 53.—Preparation of diamonds. Cooling the crucible.

Only the colorless varieties are esteemed as gems—even a very slight tint of yellow detracts immensely from the

19

value. Some diamond crystals are shown in Fig. 51. The diamonds worn as jewels are cut in such a way as best to display the luster, and are not crystals.

Chemically, the diamond is extremely inert. It is not affected by any acid, nor, in fact, by any liquid reagent, and

Fig. 54a.—Diagram of electric furnace.

most substances are without action upon it, even at a red heat. At a bright-red heat it burns brilliantly in oxygen to carbon dioxide. When fused with sodium carbonate or potassium carbonate it is converted into carbon monoxide, probably according to the equation,

$$K_2CO_3 + 2C = 2K + 3CO.$$
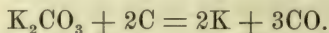
The diamond has been obtained artificially by the French chemist Moissan. In order to understand the method by which this was done, it is necessary, first of all, to know that carbon does not melt even at the very highest temperatures. At the heat of the electric arc ($3500°$) it vaporizes slowly from the solid state, and when the vapor is condensed by cooling, graphite, not diamond, is the product. Now other substances which vaporize from the solid state — arsenic, for instance — can be melted when heated under pressure. It seemed to Moissan likely that, if carbon could be obtained liquid in a similar
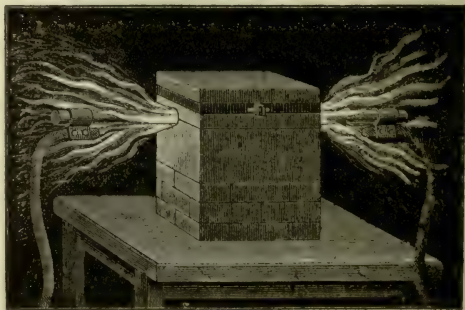

Fig. 54b.—Electric furnace in operation.

way, diamond might be produced when the liquid solidified. But it is impossible to prepare a vessel in which carbon can be melted under pressure, for no material is known which remains solid at the

temperature required. This difficulty was avoided in the following ingenious way. When iron is heated in contact with powdered charcoal in a charcoal crucible in the electric furnace, large quantities of carbon dissolve in the liquid metal. If the crucible is simply allowed to cool in the air, the carbon separates again as graphite. But if the crucible, while at the highest temperature, is plunged into water, the outside of the mass of iron is suddenly cooled and a skin or crust of solid iron is formed, inclosing the liquid interior. Iron expands when it becomes solid, and the liquid mass in the inside in solidifying expands against the inclosing crust and produces an enormous pressure. Under this pressure the carbon separates from solution in the iron, probably first in minute drops of liquid carbon, which immediately solidify to diamonds. The diamonds obtained in this way are microscopic in size and of no commercial value. Drawings of them are shown in Fig. 52. The cooling of the crucible is shown in Fig. 53, and the electric furnace in which the heating is conducted in Fig. 54. The electric furnace has been employed by Moissan in studying the effects of very high temperatures on a great variety of substances.

CHAPTER XLII

Two *compounds of carbon with oxygen* are known.

392. Carbon dioxide, CO_2, is produced when carbon burns in an abundant supply of oxygen or air, and is therefore given off abundantly from fires in which coal or wood is burned, and from the flames of gas-jets, candles, or lamps. Large quantities of the gas are also produced in the fermentation processes which are carried on in breweries, and the gas from this source is liquefied in steel cylinders, and in this form is largely used for charging mineral waters and other drinks with carbon dioxide. The bubbles which escape from all effervescing drinks consist of carbon dioxide. Carbon dioxide is produced by the oxidation of the tissues, and leaves the body chiefly through the lungs; the expired air contains about 5 per cent of it by volume. When either the air or the body is in motion this carbon dioxide is rapidly blown away; otherwise it is only slowly removed by diffusion, and it has been shown that the air in the vicinity of a man sitting quietly in a room where there are no air currents may contain as much as $\frac{1}{2}$ per cent by volume of the gas.

393. Properties of carbon dioxide.—Carbon dioxide is a colorless, odorless gas with a sharp, peculiar taste. Water dissolves about one volume of it at a pressure of one atmosphere. At higher pressures the amount dissolved increases almost in proportion to the pressure. We have seen that soda-water is water which has been charged with the gas

under a pressure of about four atmospheres. Carbon dioxide is produced in the alcoholic fermentation. From still wines the gas is all allowed to escape, the whole of the fermentation being carried on in open vessels. In champagne and other effervescing drinks a portion of the fermentation occurs in corked bottles, and the carbon dioxide dissolves in the liquid under its own pressure and escapes in bubbles when the bottle is opened; hence the effervescence.

Carbon dioxide is easily converted into a colorless liquid by pressure alone; when the liquid is allowed to escape into the air a portion of it rapidly evaporates, and this cools the rest to such an extent that it freezes to a solid which resembles snow.

394. Action upon the system.—Carbon dioxide can not be classed as a poisonous gas. The workmen in the fermenting cellars of breweries continually breathe air containing 2 per cent or more without damage. Five per cent is injurious, and much more than that rapidly causes death by suffocation. When the body is plunged in a vessel containing carbon dioxide, the head being left free so that pure air is respired, there is at first a tingling sensation of warmth over the skin. This is followed by such alarming symptoms of collapse that the experiment must be discontinued.

395. Importance of carbon dioxide in the life process.— When we studied the atmosphere we learned that the air contains about 3 parts in 10,000 of carbon dioxide, and that without this, trifling as it seems, life upon our planet would be impossible. In sunlight, in the green parts of plants, the carbon dioxide is decomposed, the oxygen returned to the air, and the carbon, with hydrogen and oxygen from water and nitrogen from other sources (p. 101), built up into complicated compounds of these four elements which serve, directly or indirectly, as food for all animals and plants. This may well be called the most important of all chemical

changes. *Its importance is due to the fact that it is the only place where energy enters the life process.* In this change the energy of sunlight is absorbed; the compounds which the plant makes contain more energy than the materials from which it makes them. Every other process which occurs in a plant, and every change without exception in the animal, is associated with a loss or dissipation of energy which appears (in the animal, especially) as motion and heat.

396. Carbonic acid.—The solution of carbon dioxide in water is acid. This is due to hydrogen ions derived from the dissociation of the acid, H_2CO_3, which is produced thus:

$$H_2O + CO_2 = H_2CO_3.$$
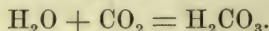
H_2CO_3 is called *carbonic acid.* It is highly unstable, and is only known in solution, but its salts, called *carbonates,* are stable and important. Some of them we have already studied. They all, when treated with hydrochloric or nitric acid, give off carbon dioxide with effervescence, and in this way we can tell whether a given substance is a carbonate or not. The action of hydrochloric acid upon calcium carbonate is the best method of making carbon dioxide. Small lumps of marble are placed in an ordinary gas-generating bottle, water enough to cover them is poured through the funnel-tube, and then strong hydrochloric acid—

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$
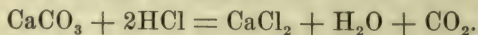
The gas is collected by downward displacement.

397. Chemical energy.—It is a familiar fact that when charcoal or coal is burned to carbon dioxide, large quantities of heat and light are produced. Now, heat and light are forms of energy, and it is clear that charcoal and oxygen separately must contain more energy than after they have combined to carbon dioxide. Sodium burns brilliantly in chlorine to salt (p. 64), and it follows from this that salt, like carbon dioxide, must contain less energy than its con-

stituents do when they exist as separate elements. If we desire to separate the salt into sodium and chlorine again, all of the energy which was given off during the combination must be restored, for energy, like matter, can not be created, and if we could decompose the salt without supplying energy to it, the energy which the sodium and chlorine would then contain would have been obtained without any expenditure—made out of nothing. By repeating the process, we could manufacture any desired quantity of energy, which is impossible.[1] The most convenient way of supplying energy to the salt is to melt it and pass through it an electric current, when it absorbs the energy of the current and separates into sodium and chlorine.

Most compounds are like salt and carbon dioxide. They contain less energy than their constituents. Hence chemical combination is usually attended by the evolution of heat, or of light, or of both. However, there are many exceptions. Many compounds—nitrogen chloride (p. 117) is a good example—contain more energy than their constituents taken separately. Such compounds are frequently explosive, because they tend to separate into their elements, at the same time liberating energy. The familiar gas acetylene is another example. It is a compound of carbon and hydrogen, C_2H_2, and when the two elements unite to form it, energy is absorbed. Hence it tends to separate again with explosion, and until this fact was learned and proper care was applied in dealing with it, accidents with it were frequent.

In ordinary life it is often necessary to store up energy. Thus, in winding a clock run by weights, we raise

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[1] Show by the same argument that when carbon is first burned to carbon monoxide and then the carbon monoxide to carbon dioxide, the same quantity of energy must be liberated as though the carbon had been burned at once to carbon dioxide.

the weights and store up energy which suffices to keep the mechanism in motion for days. In the same way electrical energy can be stored up for a time—in Leyden jars, for instance. Evidently chemical energy can be kept in the same way. We might, for instance, apply energy to the decomposition of salt, and then preserve the sodium and chlorine separately. At any desired future time the energy could be obtained again by simply bringing the two together. But it would be better to use carbon dioxide instead of salt, for it would not be necessary to preserve the oxygen, since the air furnishes a plentiful supply of this constituent. It would be quite sufficient to lay aside the carbon, and, at any time, the energy spent in decomposing the carbon dioxide could all be recovered by simply burning the carbon in the air.

Chemical energy is the great form in which energy is stored away for practical purposes. It has this great advantage, that it can be preserved for any length of time without much loss, while light, heat, and other forms of energy are rapidly dissipated. The chief substances employed as storehouses of chemical energy are, first, impure forms of carbon (charcoal, coke, and coal), and second, various compounds and mixtures containing carbon and hydrogen—wood and petroleum, for instance. It is not necessary for us to start with carbon dioxide and supply energy to it to decompose it, for this has been done for us by the plants of the coal-forming period (p. 272), which absorbed the energy of sunlight and stored it up as chemical energy. This is a remarkable instance of the permanence of chemical energy. Whether we burn coal or wood, the energy which appears is derived from sunlight. The only difference is that in the case of wood the energy was stored up quite recently, while the energy of coal is derived from the sunshine which fell upon plants which grew hundreds of thousands of years ago.

398. **Carbon monoxide**, CO, is produced when carbon dioxide comes into contact with red-hot carbon. When a slow stream of carbon dioxide is passed through a wide glass tube about 60 cm. long full of lumps of charcoal and
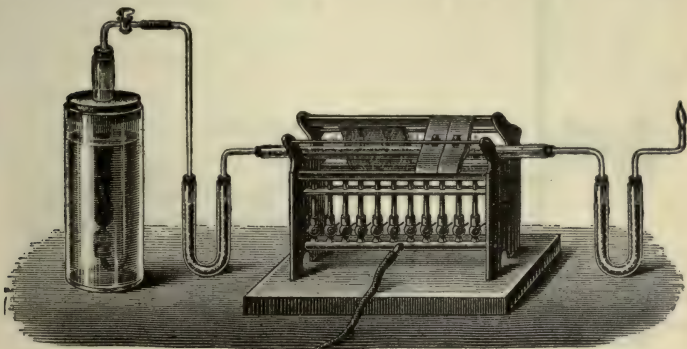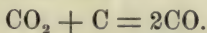

Fig. 55.—Production of carbon monoxide from carbon dioxide and carbon.

heated to redness in a furnace, almost pure carbon monoxide issues from the tube (Fig. 55).

$$CO_2 + C = 2CO.$$

This reaction occurs in an ordinary coal fire. The oxygen which enters below, at the grate, combines with the carbon to CO_2. This, as it rises through the glowing coal above, is converted into carbon monoxide, which finally, when it reaches the top, burns again to carbon dioxide at the expense of the oxygen of the air, producing the blue flame which plays upon the surface of the coal.

Carbon monoxide is usually made in the laboratory by heating oxalic acid, $H_2C_2O_4$, with strong sulphuric acid.

$$H_2C_2O_4 = H_2O + CO_2 + CO.$$
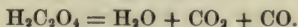
The water produced is retained by the sulphuric acid. A mixture of equal volumes of CO and CO_2 escapes, and this is passed through a wash-bottle containing potassium hydroxide, KOH, which absorbs the CO_2. The CO passes on and is collected over water (Fig. 56).

399. Properties.—Carbon monoxide is a colorless, odorless gas, very slightly soluble in water and difficult to liquefy. In air or oxygen it burns with a pure blue flame
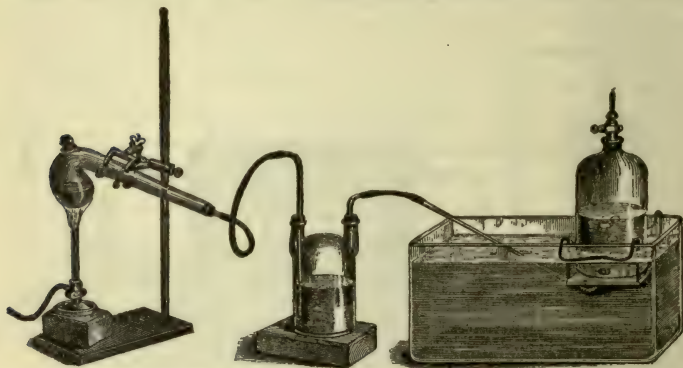

FIG. 56.—Preparation of carbon monoxide.

to carbon dioxide. It is very poisonous, $\frac{1}{2}$ per cent in air being rapidly fatal to all animals, and much less than that if the inhalation is prolonged. This is due to the fact that it combines with the hæmoglobin of the red blood-corpuscles, producing a stable compound and preventing them from doing their work of carrying oxygen about the body. Death by carbon monoxide poisoning is therefore nothing but suffocation brought about in an unusual way.

If an animal is put in air under a pressure of ten atmospheres, as much as 6 per cent of carbon monoxide can be mixed with the air without causing any symptoms of poisoning. This is because, at the high pressure, enough oxygen dissolves in the plasma of the blood to supply the needs of the tissues, so that the fact that the corpuscles no longer act as oxygen-carriers makes no difference.

400. Considerable quantities of carbon monoxide are contained in coal gas, and still larger quantities (40 per

cent or more) in *water gas*, which is made by injecting steam into a mass of red-hot coal,

$$H_2O + C = CO + H_2,$$

and which is largely mixed with coal gas at present in the illuminating gas supplied to most cities. Water gas, as the equation shows, is a mixture of carbon monoxide and hydrogen.

401. **Carbon disulphide,** CS_2, is made by throwing sulphur into a cast-iron cylinder full of charcoal heated to redness (Fig. 57). It is liberated as vapor which is condensed by cooling. It is a colorless liquid, denser than water, in which it is almost insoluble. When pure its odor is faint and rather pleasant, but it usually contains impurities which impart to it a disgusting smell. It inflames with extreme
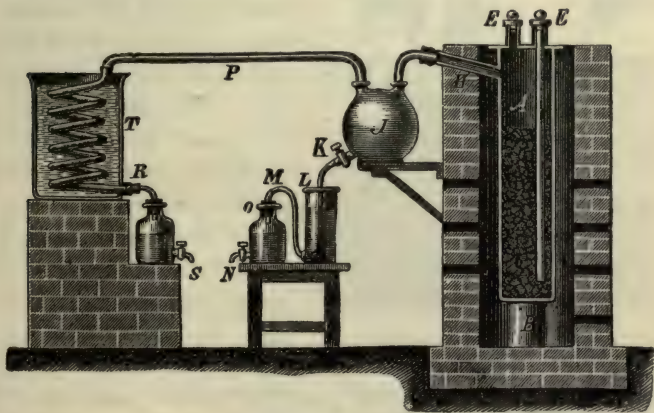

Fig. 57.—Manufacture of carbon disulphide. *A*, cylinder of charcoal ; *J*, empty vessel in which the CS_2 partly condenses ; *T*, condenser.

readiness and burns to carbon dioxide and sulphur dioxide. Its vapor is somewhat poisonous, and the workmen engaged in its manufacture suffer from disorders of the nervous system.

CHAPTER XLIII

SOME CARBON COMPOUNDS

402. **Methane**, CH_4.—When the mud at the bottom of a swampy pool is stirred, bubbles of gas rise to the surface. With the help of an inverted bottle filled with water and a funnel to catch the bubbles, it is easy to collect some of the gas (Fig. 58). In this way we can ascertain that it is colorless and combustible, burning with a pale yellow flame. It is methane, CH_4, the simplest compound of carbon and hydrogen. It is also called *marsh gas*.

Fig. 58a.—Collecting marsh gas.

Methane can be made artificially in various ways, one of which is to mix hydrogen sulphide, H_2S, with the vapor of carbon disulphide, CS_2, and pass the mixture over red-hot copper. The copper combines with the sulphur, forming Cu_2S, and the carbon and hydrogen unite, thus:

$$8Cu + CS_2 + 2H_2S = 4Cu_2S + CH_4.$$
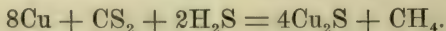
When methane is burned, the carbon is converted into carbon dioxide and the hydrogen to water. The same two products are obtained when other compounds containing

carbon and hydrogen are burned. The chief results of the burning of a candle, an oil lamp, or a wood fire are, therefore, carbon dioxide and water. Anthracite coal, which contains almost no hydrogen, produces chiefly carbon dioxide. The ash which is obtained by the burning of coal is simply incombustible mineral matter which existed originally in the fuel, and is not a product of the combustion.
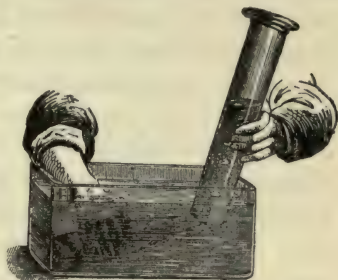
The slow conversion of vegetable matter into coal has been referred to (p.

FIG. 58b.—Transferring marsh gas to cylinder.

273). Methane is produced in this process, and it frequently escapes in large quantities from beds of bituminous coal. Mingling with the air of the mine it forms the extremely dangerous explosive mixture which miners call *fire-damp*.[1] The carbon dioxide produced by the explosion is suffocating, and forms the "choke-damp" or "after-damp" which is likely to suffocate those whom the explosion has left alive, and is especially dangerous to rescuing parties.

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[1] Like methane, every combustible gas and vapor forms an explosive mixture with air. Thus, if a cylinder is filled with illuminating gas and lighted, it burns quietly, because it can only burn at the surface of separation between the gas and air; but if the gas is mixed with the proper quantity of air, it explodes when a flame is applied because the combustion extends instantly through the whole mass. For this reason substances which give off combustible vapors, like ether, gasoline, and naphtha, should never be used when a flame or a fire is anywhere in the neighborhood. Even combustible solids, like coal-dust and flour, when suspended in air produce explosive mixtures. Destructive explosions have occurred in flour-mills from sparks from the milling stones igniting the mixture of flour and air.

403. Ethane, C_2H_6, is a colorless, combustible gas more easily condensed to a liquid than methane.

Methane and ethane are the first two members of a long series of compounds of carbon and hydrogen. The series has this peculiarity, that in every member of it the number of hydrogen atoms in the formula can be obtained by multiplying the number of carbon atoms by two and adding two to the product. Thus in ethane the number of carbon atoms is 2 and the number of hydrogen atoms is $2 \times 2 + 2 = 6$. Compounds of carbon and hydrogen are called *hydrocarbons*. What is the formula of the hydrocarbon of the methane series which contains 9 carbon atoms? The number of hydrogen atoms must be $9 \times 2 + 2$ or 20; hence the formula must be C_9H_{20}. This hydrocarbon is a liquid called *nonane*. Ordinary kerosene or burning oil consists largely of it. The higher members of the series are white, odorless solids resembling paraffine, which is a mixture containing a number of them. The highest member which has been made so far is $C_{60}H_{122}$. Crude petroleum is a mixture containing many of the hydrocarbons of this series. By distillation it is separated into various fractions, like naphtha, benzine, burning oil, and lubricating oil, all of which have important uses.

404. *Other series of hydrocarbons are known.* **Acetylene,** C_2H_2, is the first member of a series in which the number of hydrogen atoms is obtained by multiplying the number of carbon atoms by two and *subtracting* two from the product. It is interesting because it can be made in small quantities by allowing an electric arc to burn between carbon poles in an atmosphere of hydrogen. For years it was supposed to be the only hydrocarbon which could be obtained by the direct union of its elements, but very recently it has been proved that traces of methane and ethane can be made in the same way. Acetylene is a colorless gas with a peculiar odor. Its mixture with air is violently explosive, more so than is the case with other combustible

gases, so that more care is required in working with it. It is considerably used as an illuminant, especially in small places, where it would not pay to erect a large gas works, for its manufacture requires little apparatus. Acetylene is prepared on the large scale and in the laboratory by the action of water upon calcium carbide, CaC_2, calcium hydroxide (slaked lime) being produced at the same time.

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$
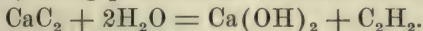
405. Calcium carbide, CaC_2, forms colorless crystals when pure, but the commercial product is a hard iron-black mass. When it comes into contact with water acetylene is liberated.

The reaction is violent, and, on the large scale, the apparatus for preparing acetylene is so constructed that powdered calcium carbide is gradually fed into water. In this way a regular stream of gas is obtained and the reaction can be readily controlled. Calcium carbide is made by heating a mixture of lime and charcoal to about 3,000° by means of an electric arc passing through the mass.

406. Substitution products of the hydrocarbons.—When chlorine acts upon methane a hydrogen atom is driven out and a chlorine atom takes its place in the molecule, forming a compound whose formula is CH_3Cl. The hydrogen, however, is not liberated. It combines with more chlorine, producing hydrochloric acid, so that the change is described by the equation—

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$
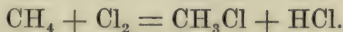
By the further action of chlorine the other three hydrogen atoms can one by one be substituted by chlorine, so that by the action of chlorine upon methane the following four compounds can be obtained:

$$CH_3Cl,$$
$$CH_2Cl_2,$$
$$CHCl_3, \text{ and finally}$$
$$CCl_4.$$
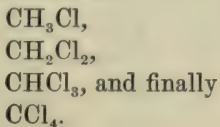
Since the compound CCl_4 contains no hydrogen to be replaced, chlorine has no action upon it. Similar compounds containing bromine and iodine can be made, and the action of chlorine upon other hydrocarbons is similar. Thus by the prolonged action of chlorine upon ethane, C_2H_6, all the hydrogen can be gradually replaced by chlorine, producing, first, C_2H_5Cl, and finally C_2Cl_6.

Such compounds are called substitution products. Only two of them are sufficiently important to be mentioned here.

407. Chloroform, $CHCl_3$, results when three of the hydrogen atoms of methane are substituted by chlorine. This is not the practical method of making it. It is prepared by a somewhat complicated reaction which takes place when alcohol is distilled with bleaching powder (p. 88). It is a colorless liquid with a peculiar fragrant odor. It is largely used for producing insensibility in surgical operations.

408. Iodoform, CHI_3, is the corresponding iodine compound. It is a yellow crystalline powder with an offensive smell. It is much employed in surgery for antiseptic dressings for wounds. Such a dressing prevents the entrance of germs from the outside into a wound, and allows it to heal without the formation of pus or other disturbing complications. The importance of this treatment is immense. Every year thousands of lives are saved by it.

409. Alcohols.—We have just seen that the hydrogen of hydrocarbons can be replaced by chlorine and other elements. It can also be replaced by groups or radicals, like OH (pp. 109–110). The compounds produced by the substitution of hydroxyl for one or more of the hydrogen atoms of a hydrocarbon are called *alcohols*. For instance, by processes which we need not describe one hydrogen atom of methane can be replaced by hydroxyl, OH. The resulting substance must have the formula CH_3OH. It is the simplest alcohol.

410. Methyl alcohol, CH_3OH, is also called *wood alcohol,* because it is produced when wood is distilled for the

production of charcoal, and this is the industrial method of obtaining it. It is a colorless liquid with an alcoholic odor. It dissolves many resinous substances, shellac, for instance, and is therefore employed in the manufacture of certain kinds of varnish. When a wooden surface is coated with a solution of shellac in wood alcohol, the alcohol rapidly evaporates and leaves the shellac as a lustrous film.

Methyl alcohol readily takes fire and burns with a hot blue flame to carbon dioxide and water. When its vapor is mixed with air and led over a hot spiral of platinum wire a kind of incomplete combustion takes place. Two hydrogen atoms are removed from the CH_4O and converted into water, while a compound, CH_2O, called formaldehyde, is left.

$$CH_4O + O = CH_2O + H_2O.$$
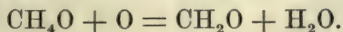
411. **Formaldehyde**, CH_2O, is a gas which can be condensed to a colorless liquid. Its odor is pungent and suffocating. It is rapidly fatal to bacteria, and is the most convenient and the most frequently employed of all disinfectants. For this purpose lamps are constructed in which formaldehyde is vaporized by heat, and the vapor escapes through a narrow tube which can be passed through the keyhole of the room to be disinfected.

412. **Ethyl alcohol**, C_2H_5OH, is the substance ordinarily called alcohol. It is a colorless liquid which freezes at —130° to a white mass. Alcohol burns easily. The flame is blue and almost non-luminous, and the products are carbon dioxide and water.

413. **Fermentation.**—The alcohol and alcoholic drinks of commerce are produced by the fermentation of liquids containing glucose, $C_6H_{12}O_6$, a substance strongly resembling ordinary sugar in composition and properties. In the presence of the yeast-plant it separates into alcohol and carbon dioxide—

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2.$$

20
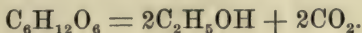
Thus, the fresh juice of apples or grapes is sweet on account of the glucose which it contains. On being allowed to stand, it ferments, carbon dioxide escapes, and the sweet taste is replaced by the alcoholic flavor of wine or cider, as the case may be. Fermentation is not produced by any vital process of the yeast plant. Yeast is killed by being soaked for a short time in a mixture of alcohol and ether, and the dead yeast so obtained on being thrown into a glucose solution produces a violent fermentation. When a mass of yeast cells is ground for a time with fine angular sand and water, so as to crush the cells and let their contents escape, and the pasty mixture is subjected to strong pressure, a liquid escapes which can be completely freed from yeast cells by filtering. This liquid, when added to a solution of glucose or ordinary sugar, throws it into energetic fermentation.
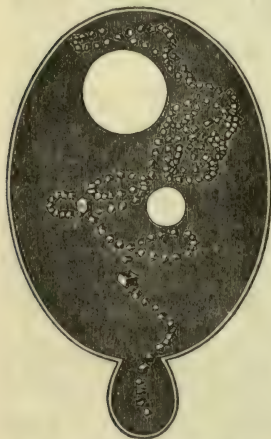

Fig. 59a.—Single yeast cell.

Facts of this kind show that what the yeast plant does is to produce and store up, in the interior of the cells, a substance which is able to act *catalytically* (pp. 42 and 49) upon the glucose and separate it into alcohol and carbon dioxide. The name zymase has been given to this substance. It is white and soluble in water, but has not yet been obtained in anything like pure condition. The yeast plant is shown in Fig. 59, greatly enlarged.

Details regarding the production of alcoholic beverages must be looked for in special works. It may be remarked that malt liquors—beer, ale, and stout—contain from 2 to 10 per cent of alcohol, and wines a somewhat larger quan-

tity, up to 20 per cent in port. Spirituous liquors—whisky, brandy, etc.—contain 50 per cent or more.

414. In order to obtain purer alcohol from fermented liquids, distillation is resorted to. The alcohol boils at a lower temperature than the water and other substances pres-
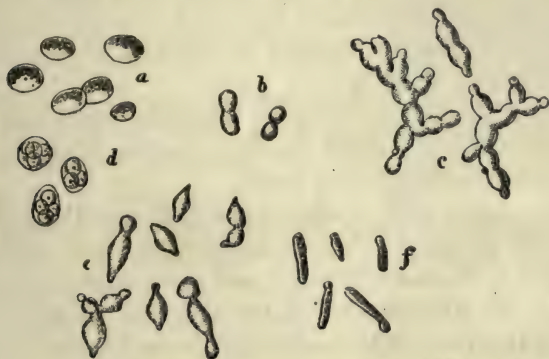

FIG. 59b.—Yeast in various stages of development.

ent, and so its vapor passes off more readily. Distilling apparatus of great perfection has been devised for this purpose, and, by means of it, it is possible to obtain a product containing less than 5 per cent of water. This is sufficient for commercial uses, but frequently, in the laboratory, alcohol quite free from water is required. This can be obtained by letting 95 per cent alcohol stand in contact with lumps of lime, which gradually slakes and absorbs the water. Then when the alcohol is distilled it is almost water-free. The last traces of water can be removed by treating the alcohol with small pieces of sodium and distilling again. Anhydrous alcohol is commonly called *absolute* alcohol. It absorbs moisture from the air and must be kept in well-closed vessels. It is quite poisonous, partly owing to the energy with which it takes water from the tissues of the body.

415. Aldehyde, C_2H_4O, is made by the gentle oxidation of alcohol—

$$C_2H_6O + O = C_2H_4O + H_2O,$$
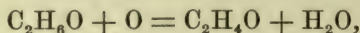
just as formaldehyde is made from methyl alcohol. It is a colorless liquid with an odor suggesting that of apples. It has no application, but a compound in which three of its hydrogen atoms are replaced by chlorine is important in medicine. It is called

416. *Chloral,* C_2HCl_3O.—It crystallizes with one molecule of water. In small doses it produces sleep, in large doses insensibility or even death.

417. Acetic acid, $C_2H_4O_2$.—We have seen that aldehyde C_2H_4O is produced by the oxidation of alcohol. Now when aldehyde is dissolved in water and the solution exposed to the air, the peculiar odor of the aldehyde disappears, and, after a time, the liquid smells and tastes like vinegar. At the same time it becomes acid to litmus and other indicators. In this process an atom of oxygen is taken from the air by each molecule of aldehyde and acetic acid, $C_2H_4O_2$, is produced. Acetic acid can be obtained—without making aldehyde—by the vigorous oxidation of alcohol—
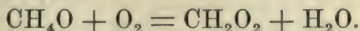
$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$
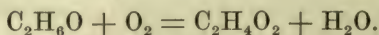
Acetic acid is, at low temperatures, a colorless crystalline solid which melts a little below room-temperature to a colorless liquid with a pungent smell. It mixes with water in all proportions. It is produced when wood is distilled, and this is the commercial source of the pure acid.

418. Vinegar is a dilute water solution containing 5 to 15 per cent of acetic acid. It also contains various flavoring and coloring constituents which differ in different vinegars, according to the mode of preparation. Any dilute alcoholic liquid—any wine or cider, for instance—will change to vinegar if exposed to the air. The change of the alcohol into

acetic acid is brought about by a peculiar micro-organism called *bacterium aceti,* which exists in the liquid. The equation above shows that a molecule of oxygen from the air is required for each molecule of alcohol. This explains the fact that the bung is removed from a barrel of cider when it is desired to allow the liquid to turn to vinegar. In the *quick vinegar process* shavings are placed in a large perforated cask and are wet with vinegar to supply the micro-organism. Wine, cider, or dilute alcohol is allowed to trickle over the shavings (Fig. 60). Thus the surface exposed to the air is

FIG. 60. — Quick vinegar process. *K,* cask; *T,* thermometer; *L,* perforated bottom; *Z Z Z,* apertures for admission of air; *E,* reservoir for collection of vinegar.

made very great, and the production of vinegar becomes rapid.

419. Like ordinary alcohol, methyl alcohol yields an acid when oxidized—

$$CH_4O + O_2 = CH_2O_2 + H_2O.$$

Formic acid, CH_2O_2, is, like acetic acid, a colorless liquid with a pungent odor. Its name is derived from the fact that it exists in ants.

Formic and acetic acids are *weak acids*—that is, they are much less separated into ions when dissolved in water than are hydrochloric or nitric acid. Hence the acid properties, which are due to the presence of hydrogen ions, are feeble.

420. **Series of carbon compounds.**—Wood alcohol and ordinary alcohol are the first two members of a *series* of alcohols which corresponds to the series of hydrocarbons, of which methane stands at the head. An alcohol corresponding to every hydrocarbon can be prepared. Those alcohols
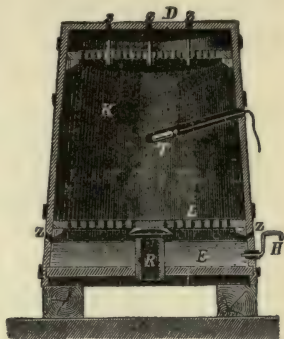
standing just above ordinary alcohol in the series are liquids with the odor of "*fusel oil,*" which is a mixture of several of them. The higher members, like $C_{30}H_{62}O$, are solids resembling paraffine.

There is also a series of *aldehydes* in which one member corresponds to each of the methane hydrocarbons and a similar series of acids. In both those series also the higher members are waxy solids.

If the student will reflect that hundreds of different hydrocarbons are known; that to almost every hydrocarbon there corresponds at least one alcohol, one aldehyde, and one acid; that the hydrogen of all these compounds can be replaced in the greatest variety of ways by chlorine, bromine, iodine, and by innumerable groups (radicals); and, finally, that there are numerous other classes of compounds which can not even be mentioned here, he will perceive that the total number of carbon compounds must be immense. In fact, about 100,000 are known at present, and thousands of new ones are being prepared every year. Most of these substances are entirely products of the laboratory, not being found in nature, though many others exist naturally in the bodies of plants and animals. Many of them have immense technical value as medicines, dyestuffs, developers, and so on.

421. The subject of the chemistry of the compounds of carbon is usually called *organic chemistry*. This name is a relic of a time when it was supposed that compounds like those we have been studying could only be produced in the organisms of plants and animals under the influence of the life process. We know now that this was an error. The carbon compounds can be made in the laboratory like other substances, but the name "organic" chemistry remains. We can take only a glance at it, for it is a vast and intricate subject, far more extensive than the chemistry of all the other elements put together.

CHAPTER XLIV

SOME ADDITIONAL CARBON COMPOUNDS—CHEMICAL PROCESSES OF THE ANIMAL BODY

422. The composition of *sugar* is described by the formula $C_{12}H_{22}O_{11}$. It will be perceived that sugar is composed of carbon, hydrogen, and oxygen, and that the last two elements are present in precisely the proportions in which they exist in water, two atoms of hydrogen to one of oxygen. A substance of this kind is called a *carbohydrate.* The carbohydrates all contain hydrogen and oxygen in the proportion in which these elements exist in water, and most of them contain six atoms of carbon in the molecule, or some multiple of that number. They are abundantly contained in plants, and make up a most important element in human food.

423. Ordinary **sugar,** $C_{12}H_{22}O_{11}$, is also called *cane-sugar* or **saccharose.** It is contained in the sap of many plants, especially that of the sugar-cane and the sugar-beet. Rock-candy is pure crystallized saccharose. Saccharose forms colorless, transparent crystals which look like cubes, but are really inclined prisms. It dissolves in about one-third its weight of water at ordinary temperatures, and is still more soluble in hot water. When carefully heated, sugar melts, and on being allowed to cool solidifies to a clear, glassy, amorphous mass, which is the basis of many kinds of candy. After a time the mass crystallizes and becomes white and opaque. When melted sugar is heated slightly above its melting-point it is converted into a sub-

stance called *caramel*. This has a somewhat bitter taste, and is not capable of crystallization. It dissolves in watery liquids, producing an intense brown color, and is largely used for coloring liquors.

424. Glucose, or **grape-sugar**, $C_6H_{12}O_6$, is abundantly contained in grapes and many sweet fruits, and in honey. It is largely manufactured by boiling starch, $C_6H_{10}O_5$, with dilute sulphuric acid. The starch takes up a molecule of water, thus—

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

Glucose is colorless and freely soluble in water. It is not so sweet as saccharose, and does not crystallize so readily. Its connection with the process of fermentation has already been referred to.

425. Starch, $C_6H_{10}O_5$, exists in plants, in round or elongated microscopic bodies called starch-granules, which differ in size and shape in different plants. Starch is white and is insoluble in cold water. When heated with water, the granules swell up and partially dissolve, forming a slimy liquid called starch-paste. Both starch-paste and solid starch are colored blue by iodine, and this is an extremely delicate test for either substance. The molecular weight of starch can not be determined with our present methods. $C_6H_{10}O_5$ is merely the simplest formula which will describe its chemical composition. The real formula is certainly a multiple of this, probably a very large multiple. This remark applies also to

426. Cellulose, $C_6H_{10}O_5$, which is the substance of which the fiber of plants consists. Wood and cotton, for instance, are largely cellulose. The best qualities of filter paper are almost pure cellulose. Cellulose is a white, amorphous mass, insoluble in almost all liquids. It has been found in the lungs of consumptives.

427. Ether, $C_4H_{10}O$, is the most important anæsthetic. It is also called ethyl oxide. The radical C_2H_5 is called

ethyl. Alcohol is ethyl hydroxide, C_2H_5OH, and ether bears the same relation to alcohol that potassium oxide does to potassium hydroxide—

Potassium hydroxide, KOH,   Ethyl hydroxide, C_2H_5OH,
Potassium oxide, K_2O.   Ethyl oxide, $(C_2H_5)_2O$.

Ether is a colorless, inflammable liquid. It is very volatile, and, when placed upon the skin, its rapid evaporation absorbs so much heat that a sensation of intense cold is felt.

When ether vapor is inhaled it produces insensibility. When the liquid is drunk, a condition resembling intoxication, but more temporary, results. Ether-drinking is a vice somewhat similar to alcoholism, but still more serious in its results. It is especially prevalent in Ireland.

428. Oils and fats.—Soap.—There is a whole series of acids, beginning with formic and acetic acids. The higher members are waxy solids. Two of these higher members are specially important. They are palmitic acid, $C_{16}H_{32}O_2$, and stearic acid, $C_{18}H_{36}O_2$. We must mention also *oleic acid*, $C_{18}H_{34}O_2$, which is a liquid. These three acids are called the *fatty acids,* because, in chemical combination with glycerin, they make up the chief animal and vegetable oils and fats.

Soaps are made by boiling fats or oils with a solution of sodium hydroxide, NaOH. The result of this operation is to produce, first, glycerin, and second, the sodium salts of the three acids mentioned above. The latter make up the soap. Soap is therefore composed of *sodium palmitate, sodium stearate,* and *sodium oleate.* If more sodium hydroxide was taken than was needed to act upon the fat, the soap will also contain NaOH. This makes the soap unfit for use upon the skin. The chapping and bleeding of the hands in winter is often due to the use of soap of this kind. The presence of sodium hydroxide can easily be detected by pour-

ing over a freshly cut surface of the soap a warm alcoholic solution of phenol phthalein. If the surface becomes blood-red, the soap contains too much sodium hydroxide and should not be used, but if it remains colorless, or turns only faint pink, it is nearly free from it.

429. **The albumins or proteids.**—Albumin or proteid is a name given to a class of substances all of which contain carbon, hydrogen, oxygen, and nitrogen. Most of them contain sulphur and a few contain iron. They are usually insoluble in water, though soluble in solutions of certain salts. When heated they decompose, carbon being left, and a complex mixture of gases and vapors given off. This mixture contains water, carbon dioxide, and ammonia, as well as many other substances, and possesses the unpleasant odor of burned horn or burned feathers. The proteids are never-failing constituents of the organisms of animals and plants. Muscular tissue, for instance, and egg-substance are chiefly composed of them.

Proteids are an absolutely necessary constituent of human food. It is impossible to support life on a diet which does not contain them. Lean meat, eggs, cheese, peas, and beans are examples of foods rich in them. Life can be sustained for a long time by food consisting chiefly of proteids, but such a diet is very unwholesome.[1]

The other two important constituents of foods are fats and carbohydrates. Cream and the fat of meat are examples of food rich in fats, while rice, bread, and potatoes contain large quantities of carbohydrates, chiefly starch.

430. **The chemical processes of the body.**—Broadly speaking, we may say that the proteids are the tissue-forming foods, while the fats and carbohydrates are burned to pro-

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[1] It is a remarkable fact that some proteids are extremely poisonous. Thus the poisonous constituents of the venom of snakes consist of substances that are very closely similar, chemically, to the white of egg.

DIMITRI IVANOVITCH MENDELEJEFF

B. Siberia, 1834.

Discoverer of the periodic law.

duce heat and the energy of motion. The products of this burning are water and carbon dioxide. It takes place in the muscles and other solid tissues of the body—not in the blood—but the arterial blood brings the oxygen for the combustion and the venous blood carries away the carbon dioxide. We must not conclude from this that arterial blood contains no carbon dioxide and venous blood no oxygen. The brightest arterial blood contains more carbon dioxide than oxygen, and the darkest venous blood—even the blood of a suffocated animal, which is nearly black—still contains much oxygen. But the blood of the arteries contains half as much oxygen again as that of the veins, and the venous blood contains about one-fifth more carbon dioxide than the arterial.

The oxygen of the blood is mainly carried by the red corpuscles, only a trifling amount being dissolved in the plasma. The red coloring matter (hæmoglobin) of the corpuscles carries the oxygen in a state of loose chemical combination.

This is important, for if the oxygen was simply dissolved in the blood, its quantity would be directly proportional to the pressure of the gas on the liquid. Hence it would be impossible to climb high mountains, or to ascend in balloons to elevations where the pressure of the air is small, for suffocation would result, and even the natural variations in pressure at the surface of the earth might cause grave disturbances of the oxygen supply to the tissues. On the other hand, working in air under pressure—for instance, in caissons, in bridge-building, or in diving-bells—would supply the organism too abundantly with oxygen and produce difficulties of another kind. As a matter of fact, no great reduction in the oxygen of the blood occurs until the air-pressure is reduced to about one-third of its ordinary amount. Then the compound of oxygen and hæmoglobin decomposes and symptoms of suffocation appear.

The carbon dioxide of the blood is mainly in the plasma, only about one-third of it being in the red corpuscles. Venous and arterial blood contain about the same quantities of nitrogen and argon. Nothing is known about the function of these two gases in the body.

The influence of light on the chemical processes of *plants* has been discussed. We know that the decomposition of carbon dioxide in the leaves, the return of oxygen to the air, and the building up of complex organic compounds, like starch, sugar, and proteids, can not occur in the absence of sunlight. Light has a similar though smaller effect upon the chemical changes of the animal. Experiment leaves no doubt, for instance, that all the complex chemical changes through which food passes in the human body, and which result finally in the production of tissue, motion, and heat, are stimulated by light, and are distinctly retarded when the body is placed in perfect darkness.

What is the chemical distinction between plants and animals? This is an interesting question, because the chemical distinction is the only one which will hold good in all cases, especially in considering microscopic life. A plant takes its carbon from carbon dioxide, its hydrogen and oxygen mainly from water, its nitrogen from ammonia, nitric acid, and various nitrates, its potassium, sodium, phosphorus, and so on, from the soil. The raw material which the plant takes consists therefore of simple chemical compounds, and out of these it builds up starch, proteids, and other substances of great complexity. *This kind of chemical work is impossible for the animal. It must have its proteids and carbohydrates supplied to it ready formed.* And its finished products consist of carbon dioxide, water, and other comparatively simple substances which are again fit to become the food of plants.

CHAPTER XLV

THE PERIODIC LAW

431. Arrangement of the elements in series.—Omitting hydrogen, let us arrange the elements in the order of increasing atomic weights. Here are the first fourteen:

Lithium Li = 7	Beryllium Be = 9	Boron B = 11	Carbon C = 12	Nitrogen N = 14	Oxygen O = 16	Fluorine F = 19
Sodium Na = 23	Magnesium Mg = 24	Aluminium Al = 27	Silicon Si = 28.5	Phosphorus P = 31	Sulphur S = 32	Chlorine Cl = 35.5

Lithium is a metal very similar to sodium, fluorine is a gas which resembles chlorine very closely and is the strongest of all the non-metals. The elements between the two are intermediate in character: any element is more non-metallic than the element to the left of it. Thus in passing from lithium to the right there is a gradual loss of metallic properties, which finally, when we arrive at fluorine, is complete.

Now the next element in order is sodium (Na = 23), one of the strongest of the metals chemically. There is no gradual transition from fluorine to sodium. We pass at once from the strongest non-metal to one of the most positive of the metals. There can be no doubt that sodium belongs in the same group with lithium, for the two resemble each other in a remarkable way. This is true also of the elements which follow sodium in the second line; each is like the one above it in the first line. Magnesium is similar to beryllium, aluminium to boron, and so on. This

similarity is greater at the ends than in the middle of the table. Sodium is more similar to lithium and chlorine to fluorine than aluminium is to boron or silicon to carbon. Yet the similarity between these middle elements is great enough to show that they belong together.

432. The " law of octaves."—Thus these two sets of seven elements each exhibit a relationship like that of two octaves in music:

1st octave	C D E F G A B
2d octave	c d e f g a b

In fact, when this remarkable arrangement of the elements was first brought forward, it was called the " law of octaves " for that reason. The properties of the elements change with increasing atomic weight, and the change is a *periodic one*—that is, similar elements occur again and again as the atomic weight increases, very much as the values of the sine of an angle repeat themselves when the value of the angle increases.

This periodic change in properties with increasing atomic weight is the root-idea of the periodic law, and, if all the elements behaved like the first fourteen, the whole matter would be very simple. We should arrange the elements in the order of increasing atomic weights in horizontal lines, each containing seven elements, and those elements falling in the same vertical line would belong together and show similarity in properties. We shall see at once that the real state of things is more complicated than this.

433. Long and short periods.—The set of elements from lithium to fluorine we call the first short period, and that from sodium to chlorine the second short period. The next seventeen elements in the order of increasing atomic weights are the following:

1	2	3	4	5	6	7	8
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	
K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	Iron Cobalt Nickel
Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Fe=56 Co=59 Ni=58.7
Cu=63.5	Zn=65.5	Ga=70	Ge=72	As=75	Se=79	Br=80	

This set begins, as we should expect it to, with a metal (potassium) whose similarity to sodium and lithium is very great. Farther along in the first line we discover that we have here a different arrangement from that of the short periods. Chromium is not very similar to oxygen and sulphur in whose vertical group it falls, for it is much more metallic in character; while the similarity between manganese, on the one hand, and fluorine and chlorine on the other, is remote, manganese being, in most of its chemical conduct, a metal. Yet, though in both cases the elements differ from the corresponding ones of the short periods, there are still some striking points of similarity which justify us in classing chromium with oxygen and sulphur, and manganese with fluorine and chlorine. One important difference between this arrangement and that of the short periods is, then, that at the seventh element—manganese in this case—the metallic properties have only partially but by no means completely disappeared. Further, the next metal, iron, is by no means a metal like sodium, as it should be if it stood at the beginning of a new short period. From manganese (Mn = 55) to copper (Cu = 63.5) through the three elements of the eighth column—iron, cobalt, and nickel—there is a gradual increase of metallic properties and not a very great increase, for copper, though a more positive metal than manganese, bears no comparison to potassium in that respect. In the last seven elements, from copper to bromine (Br = 80), there is a gradual and complete disappearance of the metallic characteristics. Bromine is an unmistakable non-metal, and belongs in the same group as fluorine and chlorine.

This set of seventeen elements is called the first long period, and the general plan on which a long period is built is this: First stands one of the strongest positive metals chemically, and, following it, six elements in which the metallic qualities diminish, but do not completely disap-

pear, so that the seventh element, like manganese, shows mixed metallic and non-metallic characters. The position of the three following elements is peculiar. Their atomic weights lie near together (compare the atomic weights of iron, cobalt, and nickel), and they resemble each other, but we can trace through them a gradual increase in metallic properties, so that the first member of the second set of seven—copper, for example—is more metallic than the last member of the first set of seven—manganese, for instance. Finally, through the remaining six elements the metallic properties gradually and completely vanish, so that the last member of the long period is, in all respects, a non-metal.

434. **Grouping of the elements according to the periodic law.**—The complete arrangement of the elements according to the periodic law is given in the table. The vertical columns are called groups, and the student will be prepared to find that elements in the same group resemble each other. It is convenient to divide each group into two subgroups, and the resemblance between members of the same subgroup is especially close. Thus, in the first group, the members of the sodium group (subgroup A), lithium, sodium, potassium, rubidium, and cæsium, resemble each other far more than they resemble the elements of the copper group (subgroup B), copper, silver, and gold. The elements of the first and second groups are all metals, and so are all those of the third group except the first one—boron. With this exception the non-metals are all contained in the fourth, fifth, sixth, and seventh groups, and the strongest non-metals stand at the top, for in a subgroup composed of non-metals the non-metallic properties decrease with increase of atomic weight. This is well shown by the fact that no non-metal is known having a higher atomic weight than that of iodine ($I = 127$). In a subgroup of metals the reverse is usually true—the higher the atomic weight the more marked the metallic properties.

Arrangement of the elements according to the periodic law.

Period	Group 1 (Sodium Group / Copper Group)	Group 2 (Calcium Group / Zinc Group)	Group 3 Aluminium Group	Group 4 Carbon Group	Group 5 Nitrogen Group	Group 6 Oxygen Group	Group 7 Halogen Group	Group 8 — Including the Iron Group, the Platinum Group and the Argon Group			
1st Short Period	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19				Ne 20
2nd Short Period	Na 23	Mg 24	Al 27	Si 28.5	P 31	S 32	Cl 35.5				Ar 40
1st Long Period	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 58.7	
	Cu 63.5	Zn 65.5	Ga 70	Ge 72	As 75	Se 79	Br 80				Kr 82
2nd Long Period	Rb 85	Sr 87.5	Y 89	Zr 91	Cb 94	Mo 96		Ru 102	Rh 103	Pd 106	
	Ag 108	Cd 112	In 114	Sn 119	Sb 120	Te 127	I 126.85				X 128
3rd Long Period	Cs 133	Ba 137	La 138	Ce 140	Di 142		Sa 150				
				Er 166							
4th Long Period			Yb 173		Ta 183	W 184		Os 191	Ir 193	Pt 195	
	Au 197	Hg 200	Tl 204	Pb 207	Bi 208						
				Th 233		U 239					

The sodium group (subgroup A of the first group) contains those elements which manifest metallic properties in the greatest perfection, and the most positive metal of these, and, in fact, the strongest metal known, is cæsium (Cs = 133), which has the highest atomic weight in the subgroup.

435. Position of argon and the allied elements in the periodic system.—Recently there has been much discussion as to the place of argon, helium, neon, krypton, and xenon in the periodic system. All of these elements exist in the atmosphere (p. 100). They are colorless gases, and their chief distinction is complete chemical inertness—it is impossible to induce them to take part in a chemical process, and therefore we can not classify them either as metals or non-metals chemically.

Now the atomic weight of *neon* is about 20. Therefore it must follow fluorine (F = 19) and precede sodium (Na = 23) in the table and must fall in the eighth group. But fluorine is the most intense of non-metals (p. 251) and sodium one of the strongest of metals. *Neon, an element of no chemical character whatever, comes in as a natural transition between these two extremes.*

Neon being thus provided with a very satisfactory position, what about the other inert gases? In the first place it is clear that they must all belong in the eighth group, if neon is to be placed there, for they resemble it very closely. Argon, with its atomic weight of about 40, falls between the strong non-metal chlorine and the strong metal potassium. Krypton (Kr = 82) is a transition between bromine (Br = 80), a distinct non-metal, and rubidium (Rb = 85), a metal of the sodium group. Finally, xenon (X = 128) must be placed between the halogen iodine (I = 127) and cæsium (Cs = 133), the most positive of the sodium metals. Thus these elements find a natural place in the eighth group as transition elements between the strongly non-metallic

halogens and the strongly metallic elements of the first group.

436. **Uses of the periodic law.**—The student will notice at once that there is a number of gaps in the table. A gap arises when we are forced to leave a vacant space for the sake of preserving the arrangement. Thus, in the second long period, after molybdenum ($Mo = 96$) in the sixth group, the next known element in order of increasing atomic weight is ruthenium ($Ru = 102$). Now the whole chemical character of this element shows that it belongs in the eighth group, and not under manganese. Further, if we simply proceeded in order, placing ruthenium under manganese, not only ruthenium itself but every following element would be thrown out of place, and the whole latter portion of the table would be disarranged. Therefore we leave a vacant space and preserve the arrangement, believing that the place under manganese belongs to some unknown element which has an atomic weight of about 100. Thirty years ago, when the table was first published, gaps were more numerous. The Russian chemist Mendelejeff, the founder of the periodic law, gave it as his opinion that the vacant spaces would be filled by the discovery of new elements, and in several cases he predicted in detail the properties of these elements and their principal compounds from the place which they ought to occupy in the table. These predictions were verified, the properties of the newly discovered elements agreeing with Mendelejeff's statements with wonderful closeness—a striking proof that the periodic classification is a real law of nature and not a mere artificial arrangement.

437. **The periodic law is a great aid in fixing the values of atomic weights.**—Perhaps the most important use of the periodic system is to make us completely certain that the values of the atomic weights, as they are accepted at present, are very close to the correct ones. The place of an

element in the table fixes its atomic weight within narrow limits, and has often given us valuable information in this direction. Suppose a doubt to exist as to whether the atomic weight of sodium was 23 or $23 \times 2 = 46$. Then the fact that sodium is a strong positive metal and resembles lithium very closely shows at once that it belongs in the first group, and that its atomic weight must lie between that of fluorine ($F = 19$) and of magnesium ($Mg = 24$). This leaves 23 as the only possible value.

438. Defects of the periodic law.—The classification is not perfect. There is no very satisfactory place in it for hydrogen. Again, the latest atomic weight determinations indicate that in two cases an element has a slightly *lower* atomic weight than the one which precedes it in the table. Thus, nickel must follow cobalt; but its atomic weight is a little smaller, and the same is true of iodine and tellurium. These difficulties are serious and they may result in some alteration of the present arrangement, but the fundamental fact that the properties of the elements vary periodically with the atomic weights is secure.

439. From the fact that the properties of the elements vary with the quantity of matter in the atom some chemists have drawn the conclusion that the *kind* of matter is the same in all, and that all the elements are different forms of one universal substance. Mendelejeff himself is opposed to this idea, but it is difficult to deny that the periodic law furnishes a strong excuse for it.

If the student will carefully inspect the table he will perceive that the elements we have studied have all been arranged according to the periodic law. This, in fact, is the best possible classification. And the fact that the elements grouped and studied together were clearly similar to each other is positive proof of the truth of the law which furnished the classification.

CHAPTER XLVI

THE HISTORY OF CHEMISTRY

440. Development of chemical theories.—Without knowing something of the history of our science it is impossible to understand its present state, for we are likely to fall into two very serious errors: first, that of believing that the science originated all at once in the mind of the writer of the book we are reading; and, second, that of thinking that the views which happen to be held at present upon chemical subjects are absolutely true and will remain unchanged for all time. A glance at the history of chemistry will show us that the gathering of the vast wealth of facts which the science possesses began thousands of years ago, and that the theories which now aid us to arrange and remember the facts and to discover new facts, have been slowly developed from other quite different theories, and will, in all probability, be supplanted, in their turn, by others.

441. Chemical knowledge of the ancients.—Among the ancient Egyptians, Greeks, and Romans there was no systematic chemical knowledge—nothing that could be called a science. Accident, and the needs of daily life, had caused a large number of facts to become known, but no attempt was made to classify or explain them.

The name of our science is derived from the Egyptian word Chemi, which means Egypt. In that country chemistry was considered a sacred art and was studied only by the priesthood. The earliest laboratories of which we have any

record were rooms in Egyptian temples in which chemical operations were secretly carried on.

Gold and silver, which occur free in nature, were probably the first metals discovered, though copper was known before the dawn of history, and iron at a very early date. Lead was much used by the Romans for making water-pipes, and tin was also known to them, but they did not regard them as two different metals. Brass—the alloy of copper and zinc—was known in very early times, but was regarded simply as copper colored yellow. Various industries of a chemical character, for instance, dyeing and the manufacture of glass and pottery, flourished among the Egyptians, Romans, and Phœnicians. Soap was first made by the barbarous German tribes from wood-ashes and animal fat. The preparation of lime and of building-mortar from it is very ancient. Acetic acid (in vinegar) was the first acid discovered. Other compounds of carbon which have been known for more than two thousand years are sugar, starch, and oil of turpentine.

442. **The alchemists.**—*Alchemy* is the attempt to transform copper, mercury, and the other so-called " base " metals into gold and silver. This effort began in Egypt. When the Arabs conquered Egypt they acquired alchemistic ideas, which they carried with them to Spain. Thence alchemy penetrated Europe, where it flourished, particularly in Germany, for centuries, and thousands of men wasted their lives in the attempt to accomplish the impossible. Most of them were honest in their belief that the transmutation of metals was possible, but others were mere cheats who lived by trading upon the credulity of princes. Each prince had his court alchemist, and—seduced by the hope of making coinage for his realm out of alchemistic gold—expended vast sums of money in experiments which invariably failed.

Finally, when it was discovered that the alchemist was unable to accomplish what he had promised, he was dis-

missed in disgrace, or, more frequently, treated with terrible severity. A favorite mode of punishment consisted in dressing the alchemist in a garment of cloth of gold and hanging him on a gilded gallows.

The alchemists believed that the transformation of the baser metals into gold was to be accomplished by means of a substance called the " *philosopher's stone.*" The directions which they give for preparing this marvelous material are quite meaningless, but with respect to its properties they speak more plainly. It was ruby red, transparent, crystalline, and luminous in the dark. It was very dense, but brittle and easily powdered, and the powder glittered like crushed glass. Its possession conferred perfect health, and by its proper internal use life might be prolonged for many centuries. When copper or some other metal was melted in a crucible, and some of the " philosopher's stone " thrown upon it, it was completely transformed into gold.

The efforts of the alchemists to prepare this imaginary substance lasted for nearly fifteen centuries, and every imaginable material, not only of mineral, but of vegetable and animal origin, was investigated. Incidentally many facts were discovered and methods devised which have been of great value to our science. We owe to the alchemists the operations of filtration, crystallization, sublimation, and distillation, and the discovery of hydrochloric, nitric, and sulphuric acids, of arsenic, antimony, and phosphorus, and of many important salts, like silver nitrate and potassium nitrate. Most important of all, we owe to them the conviction that no element can be changed into any other; that in order to prepare gold or any other element we must start with some material which contains it. It must be remembered that this law is not self-evident. It is simply the result of experience. To a man who had no chemical knowledge the transformation of copper into gold by means

of the philosopher's stone would not be nearly as incredible as the transformation of water into oxygen and hydrogen by the electric current.

It will help us to understand how the transmutation of the metals could appear possible to the alchemists if we recall the fact that they did not regard the metals as elements, and, in fact, that the word element had not the meaning to them that it has to us. The present definition of the elements as the constituents of compounds, constituents which can be obtained in the free state, and can not be decomposed into simpler substances, was first given by the famous Robert Boyle—the discoverer of Boyle's law—in 1661. The alchemists, on the contrary, believed that the metals were compounds of mercury and sulphur. The mercury was supposed to give them their luster and the sulphur the property of being oxidized or otherwise altered when heated in the air. To any one holding this belief the conversion of one metal into another appears a very simple matter. Thus it was held that tin and lead are both compounds of mercury and sulphur. The only difference between them is that the tin contains more mercury and less sulphur than the lead. Hence it was gravely asserted and believed that lead could be transformed into tin by heating it with a little mercury in a crucible, and no one disproved the statement because our present method of investigating such matters by experiments was not yet in use. Gold and silver, on account of their strong luster and the fact that they were not affected by heat, were considered to be richer in mercury and poorer in sulphur than the other metals.

443. The doctrine of phlogiston.—Out of innumerable failures there finally emerged the conviction that the object of alchemy was impossible, and that alchemistic labors were a waste of time. Then followed a period in which it was believed that " the object of chemistry is not to make gold

but to prepare medicines " (Paracelsus). During this time many new substances were prepared, and everything, both new and old, was tested to see whether it could be used in the cure of disease. In this way many results of great value, both to chemistry and to medicine, were obtained.

Finally, about the middle of the seventeenth century, chemistry took rank as a distinct science, with aims and methods of its own, and the first problem to which chemists turned their attention was the explanation of the striking phenomena of combustion. What happens when sulphur or a candle burns, or when a metal is heated in the air and passes into a lusterless, earthy mass then called the *calx*? It seemed clear that the cause of combustion must be the same in all cases, and that all combustible bodies must contain a common constituent which made them combustible. To this imaginary substance the name *phlogiston* was given. Thus zinc, for example, is a compound of the white substance, zinc calx—which we now call zinc oxide—with phlogiston. When the zinc is heated strongly the phlogiston escapes into the air, producing flame, and there remains in the vessel the other constituent of the zinc, a white mass of zinc calx. So when copper is heated the phlogiston of the metal escapes and copper calx, which is black, remains behind. The metals do not produce calxes when all air is excluded because the phlogiston can not escape.

A substance like charcoal, which burns away leaving little or no residue, was regarded as composed of pure or nearly pure phlogiston. Thus it is easy to see why charcoal, when heated with the calxes (oxides) of the metals, converts them into metals. It simply restores the phlogiston which was lost when the metal was heated in the first place. Thus tin is a compound of tin calx (tin oxide) with phlogiston, and when tin is heated the phlogiston escapes and white lusterless tin calx is left. But when tin calx is mixed with charcoal—which is nearly pure phlogiston—and heated, the

charcoal restores the phlogiston which had escaped, and metallic tin is again obtained.

For a long time the phlogistic idea appeared to furnish a satisfactory explanation of combustion phenomena, but during the eighteenth century it gradually became evident that there were grave defects in it. Thus there are some calxes, like calx of mercury (mercuric oxide), which when heated alone are converted into metal, without the aid of charcoal or any other substance. It is not clear whence the phlogiston comes in such cases. But the great difficulty was the fact that all experiments showed that the calxes weighed more than the metals from which they were made. Clearly, if the metal is a compound of the calx with phlogiston, it should weigh more than the calx.

444. The work of Lavoisier.—This objection was a fatal one; nevertheless the theory of phlogiston continued in favor until Priestley's discovery of oxygen supplied the key to the correct explanation of combustion. Priestley himself never grasped the magnitude of his discovery. The explanation of the *rôle* which oxygen plays in combustion, in the oxidation of metals, and in respiration was the work of the great French chemist Lavoisier. It was Lavoisier who caused the downfall of the theory of phlogiston and who set up in its place our present views.

The law of the indestructibility of matter had been accepted without proof by many chemists, but we owe to Lavoisier the first experimental evidence of it. He sealed up a quantity of tin in a retort, and, after careful weighing, heated the tin for a long time. When the tin had combined with the oxygen of the air in the vessel he weighed again and found the weight unchanged—there had been no creation or destruction of substance in the burning of the tin. Upon opening the vessel it was easy to show that a portion of the air had disappeared and that the remainder was incapable of supporting combustion. This plan of heating substances

in closed vessels to show that chemical changes produced no alteration in weight was repeatedly employed by Lavoisier, and has been much used recently for the same purpose.

Lavoisier was guillotined upon baseless and absurd charges during the Reign of Terror in 1794.

445. The atomic theory. Determination of atomic weights.—Lavoisier and his predecessors had accepted the *law of definite proportions*—that the composition of a compound is always the same—without question. Proust first established this law by convincing experiments in the opening years of the nineteenth century. About the same time (1804) occurred another event of great importance to our science—the statement of the chemical atomic theory by John Dalton.

The idea of atoms was not new. It is almost as old as thought itself, and various ancient Greek philosophers, especially Democritus, had framed theories of the universe based upon it. Further, the view that the atoms of two different elements might unite to form the particles of a compound had been stated by Boyle and employed by Lavoisier. What Dalton did was to recognize for the first time that the atoms must have definite relative weights (pp. 94–96), and that by analyzing chemical compounds it is possible to determine these weights.

Chemists at once attacked the task of determining the atomic weights. The leader in this work was the Swedish chemist Berzelius. With tireless industry and wonderful skill he accomplished the immense labor of determining the atomic weights of the elements known at that time. It is difficult for us at present to realize the conditions under which Berzelius and other chemists of that time worked. Scarcely anything which Berzelius needed could be purchased. Everything had to be made. Even the three ordinary acids had to be prepared or purified in the laboratory.

There was no gas, and the alcohol which Berzelius needed for his spirit-lamps he was compelled to distill himself. Nevertheless the atomic weights were determined with an accuracy which, considering the state of the science at that time, is remarkable. All of the determinations have been repeated by various chemists, and the atomic weights which we now possess, particularly for the more abundant elements, are quite exact.

We owe to Berzelius also our system of chemical symbols and formulas, a system which has immensely assisted the progress of the science.

446. Throughout the first quarter of the nineteenth century the chemical compounds of the plant and animal kingdoms were considered to be totally different in character from other substances. They were supposed to be produced in the organism under the influence of something called "vital force," the result of which was to give rise to a class of substances distinct in character from laboratory products. It was even supposed that the simple laws of definite and multiple proportions (pp. 33 and 96) did not apply to organic substances.

In 1828 Wöhler prepared artificially *urea*, a substance of the composition of CON_2H_4, found in the urine, which had hitherto been met with only as a product of the chemical processes of the animal body. Since then thousands of similar substances have been made, and there is no longer any doubt that the same laws hold good for all chemical compounds, and that all of the complicated products of the animal and plant organism will be made artificially. Many of them are now manufactured on a large scale. Thus the madder-plant is no longer grown for dyeing purposes, because its coloring matter, *alizarin*, can be made much more cheaply by chemical methods. Artificial indigo is replacing the natural product.

447. The statement of the *periodic law* by the Russian

chemist Mendelejeff was made in 1869. It has been of immense value to the science.

Among the achievements of the closing years of the nineteenth century may be mentioned the investigation of the nature of solutions (pp. 127–131), the invention of methods of determining the molecular weight of *dissolved* substances, the work of Moissan with the electric furnace upon high temperatures (p. 276), and the discovery of argon and the related elements—remarkable on account of their complete chemical inertness.

448. **The practical and educational value of chemistry.** —Chemistry is well worth studying, simply from the standpoint of culture, for the sake of the mental development and insight into the nature of things which it gives. But the immense practical benefits which the science has conferred and will confer upon mankind give it claims of another kind to attention. As a result of the work of the chemist the widespread poisoning of the middle ages has ceased, the productive capacity of our fields is doubled, the ill-smelling and useless coal-tar has become an inexhaustible source of delicate perfumes, brilliant dyes, and invaluable medicines, surgical operations are performed without the horrible suffering which once characterized them, and every branch of industry receives assistance which rapidly becomes indispensable to its existence. What is to-day a curiosity of the laboratory is to-morrow manufactured by the ton, and has become the luxury or necessity of thousands. No better investment can be made by a country than the proper equipment of chemical laboratories for investigation and instruction. To say that money thus spent will return a thousand-fold is a totally inadequate statement. And to ask that an insignificant fraction of the wealth which our science has created shall be applied to its further development and diffusion is a very modest request.

APPENDIX

Abundance of the Elements in Nature

LIST OF THE ELEMENTS IN ORDER OF ABUNDANCE.	Composition of the solid crust of the earth.	Composition of sea-water.	Composition of the earth's crust, including the ocean and the atmosphere.
	Per cent.	Per cent.	Per cent.
Oxygen..................	47.29	85.79	49.98
Silicon	27.21	....	25.30
Aluminium	7.81	....	7.26
Iron....................	5.46	....	5.08
Calcium	3.77	0.05	3.51
Magnesium	2.68	0.14	2.50
Sodium.................	2.36	1.14	2.28
Potassium	2.40	0.04	2.23
Hydrogen	0.20	10.67	0.94
Titanium	0.33	....	0.30
Carbon	0.22	....	0.21
Chlorine...............	0.01	2.08	0.15
Phosphorus.............	0.10	....	0.09
Manganese	0.08	....	0.07
Sulphur	0.03	0.09	0.04
Barium.................	0.03	....	0.03
Nitrogen	0.01	....	0.02
Chromium	0.01	....	0.01
	100 per ct.	100 per ct.	100 per ct.

The crust of the earth does not contain as much as 0.01 per cent of any one of the remaining 60 elements. The entire 60 make up but a small fraction of 1 per cent.

INDEX

(5)

THE END

ELEMENTARY CHEMISTRY

PART II
EXPERIMENTAL WORK

BY

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PREFACE

In the preparation of the Laboratory Manual I have tried to make the directions as complete and clear as possible. Wherever there is any danger in carrying out an experiment, the necessary precautions are explicitly stated, even at the cost of some repetition.

Most of the experiments—but not all of them—are intended for individual laboratory work. This is a matter which will vary with the equipment of the school and the size of the classes. The following is a list of the numbers of the experiments which I have found to be better fitted for lecture-table or laboratory demonstrations than for individual work, but it is merely the result of my own experience, and is not intended to have any prescriptive implication :

Numbers 7, 9, 10, 27, 31, 40, 49a, 50, 51, 60, 128, 129, 133.

The questions placed after each chapter are based partly on the laboratory exercise and partly on the corresponding chapter of Part I. The student should not fall into the error of supposing that his own experimental work supplies all the necessary data for answering them.

R. H. B.

Central Manual Training School, Phila.

CONTENTS*

* Chapters correspond to those in Part I.

ELEMENTARY CHEMISTRY

PART II

EXPERIMENTAL WORK

General suggestions.—Chemical laboratory work is by
no means free from danger. The eyes, especially, are
likely to be injured if the work is not done with proper
care. The secret of safety is the accurate observance of
the directions given for the performance of the experi-
ment. Before carrying out an experiment the student
should carefully read the directions and should observe
them scrupulously, asking for information on any points
which are not clear.

Neatness is essential to success. Experiments made in
dirty test-tubes, beakers, or mortars, are worthless, mis-
leading, and often dangerous. Every piece of apparatus
employed must be spotlessly clean and must be cleaned
carefully after the work is done.

*The sinks in the laboratory tables are intended only
for liquids. Solids, like bits of broken glass, match-sticks,
and paper, must never be thrown into them.*

The student must be continually on his guard against
the tendency—almost universal with beginners—to take
too much of the various chemicals required in the experi-
ments. One objection to this is waste of material. An-
other is waste of time, for it always requires a much longer
time to carry out a process with a large quantity of sub-
stance than with a small quantity. Finally, there are many

1

experiments which are perfectly safe on the small scale
but become highly dangerous when the quantity is in-
creased.   As a rule, the quantity of material to be taken
is indicated in the directions, and nothing but loss of time
and danger result from taking more.   Where no amount
is stated, take the smallest that you can conveniently work
with.

Anything which is spattered into the eyes must be re-
moved instantly by copious washing with water.   Acid
splashed upon the skin should be washed off at once with
abundant water, and if a wound has resulted from its ac-
tion, it should be treated with a paste made of sodium
acid carbonate (baking soda) and water.   The same paste
may be applied to burns.

PRELIMINARY EXERCISE.—THE BUNSEN BURNER; GLASS
ROD AND TUBING

A. **The Bunsen burner.**—Examine the burner.   Close
the holes at the base and light it.   Hold a piece of glass

FIG. 1.

tubing in the flame for a time.   Open the
holes and describe the change which the flame
undergoes.   Hold a piece of glass tubing in
this flame.   Which flame is hotter?   Which is
cleaner?   Which is least affected by drafts?
What is the cause of the difference between
the two flames?   Which is the hottest part
of the blue flame?

Is the blue flame hollow or solid?   Ob-
tain facts to answer this question by thrust-
ing a match-stick horizontally through the
flame near the burner.   Support a match by means of a
pin, as shown in Fig. 1, and light the burner.   Remove
the match, and hold in the center of the blue flame near the
burner one end of a glass tube open at both ends.   The
tube should be inclined obliquely upward.   Hold a lighted

match to the upper end of the tube. What does this show regarding the nature of the interior of the flame?

Open the holes at the base as wide as possible, and gradually turn off the gas until the flame strikes back. Why does the flame only strike back when the current of gas up the chimney becomes slow? While the flame is still burning below, turn on the gas and light it above. Is this flame suitable for use? How can the burner be made to give the blue flame again?

The flame must never be allowed to burn below, since it gives off poisonous gases. Remember in using the burner that—except where high temperatures are required—a small flame is better than a large one. Do not light the burner until you are ready to use it, and always turn it down or extinguish it when it is not in use.

Take the burner apart, make drawings of the parts, and explain the function of each.
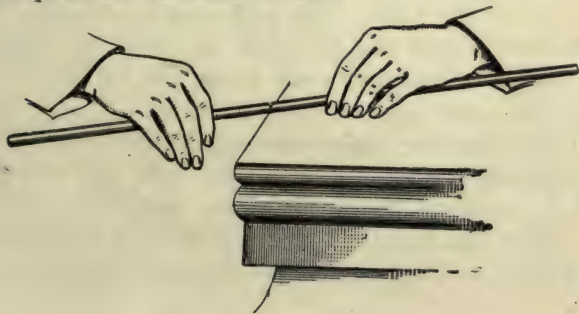
FIG. 2.

B. **Glass rod.**—With a triangular file make a notch on a piece of glass rod 15 centimeters [1] (6 inches) from the end. One sharp stroke of the file is sufficient. Holding the rod as indicated in Fig. 2 endeavor to bend it away from the notch, and it will break off at that point.

[1] Hereafter the abbreviation cm. for centimeters will be used.

Cut off three such pieces. Since the ends of the rods are jagged and inconvenient to handle, round both ends of each rod by holding it in the Bunsen flame and rotating the rod gently. Support the rods by the middle on your test-tube rack until they cool. (Hot glassware or hot apparatus of any kind must never be laid on the desk or put away under it.)

C. **Glass tubing.**—Examine a piece of hard and a piece of soft glass tubing. Carefully note and record the differences in appearance between them. Select for yourself a piece of each kind of glass from the main stock. Cut, just as you cut the glass rod, two pieces of the soft glass, each 20 cm. (8 inches) in length. Cut one piece of hard glass tubing of the same length.

Hold the middle of your piece of hard glass tubing in the flame, turning it gently, and when it becomes red-hot, gently and slowly draw the two portions asunder. Do not twist the tubes. The pull must be straight. Let the two tubes cool and use them to study the effect of heat upon a fragment of wood (match-stick) and a little sugar.

In the same way make four sealed tubes of soft glass. The temperature required is not so high, and the glass must be removed from the flame before drawing it out. Then the thin middle portion must be returned to the flame and melted and the two tubes formed drawn apart.

Use these tubes for studying the effect of heat upon a little paper, a crystal of iodine, a fragment of sulphur, and a small piece of starch. *Never heat anything in a tube sealed at* BOTH *ends, since this would cause explosions.* Soft glass tubing is used for all ordinary purposes; and hard glass tubing—which is much more expensive and more difficult to manipulate—only when high temperatures are to be applied.

Bending glass tubing.—For bending use the flame of a wing-top burner, never the Bunsen flame. Hold the tube—which should be of soft glass—so that the flame heats as long a portion as possible, and rotate it so that it is evenly heated. When sufficiently hot remove it from the flame and make the bend. When the tube is perfectly cold remove the soot by wiping the outside with paper.

In this way, bend a soft glass tube into an acute angle (Fig. 3). Select a piece of soft glass tubing about 50 cm. (20 inches) long and bend it twice at right angles
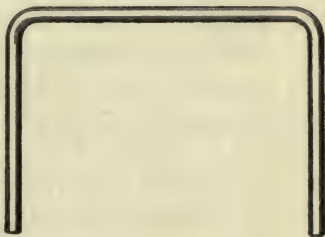
Fig. 3.   Fig. 4.

(Fig. 4). This must be done so that when the double bend is laid upon the table every part of it will touch the surface of the latter, or, in other words, the two limbs must be in the same plane. Round the sharp ends of the bent tube by holding them a short time in the flame—not long enough to cause them to collapse.

CHAPTER I

WATER

EXPERIMENT 1.—Place a small piece of potato in a dry test-tube. Clamp the tube horizontally and heat gently with a small flame. As soon as a positive result is obtained stop the experiment.

What is the result? Other vegetable substances would behave in the same way. Draw a conclusion regarding the existence of water in living things. Mention some vegetable products in which the presence of abundant water is evident on mere inspection.

EXPERIMENT 2.—Crush some ice in a mortar and half fill a small round-bottomed flask with it. Dry the outside of the flask carefully with a towel and clamp it about 25 cm. (10 inches) above the desk. Directly under it place a clean, dry beaker. Let the apparatus stand for an hour or more while you go on with other work. What does the result prove? How does warm air differ from cold air in its capacity for water? What is dew and how is it formed? What is humidity and how does it affect our sensations in warm weather? Suppose the flask had contained a mixture of ice and salt, what difference would have been noticed in the result? If water should suddenly cease to evaporate into the air, what changes would occur upon the earth's surface? Sketch the apparatus in your note-book.

EXPERIMENT 3.—Carefully evaporate a little faucet water to dryness in a perfectly clean porcelain dish. Is the water pure? If not, what is the source of the impurities? Evaporate a little distilled water in the same way. What is the difference?

EXPERIMENT 4.—Set up the apparatus shown in Fig. 5 and distill some water in it. The flask should be half filled with water which has been colored by ink. It must be perfectly dry on the outside, and is heated gently with a piece of wire gauze between it and the flame to avoid breakage. Before heating, connect the condenser with the water supply and pass a gentle current of water in at the lower tube, letting it run off at the upper tube into the sink. Avoid violent boiling, which would carry over the impurities into the receiver. Distill about 100

cubic centimeters [1] of water, stopping before the water in the flask becomes very low, otherwise the latter would break. Test the purity of the water by evaporating a small quantity in a perfectly clean dish.
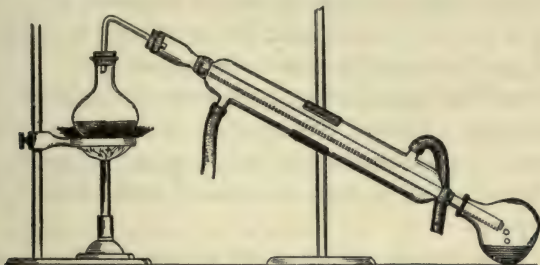
Fig. 5.

How does distillation remove the impurities from water? Can *all* impurities be removed in this way? Why is glass apparatus not used in making distilled water commercially? Make a drawing of the apparatus.

EXPERIMENT 5.—Fill a beaker with crushed ice and clamp a thermometer so that the bulb is surrounded by the mass. Notice the behavior of the mercury column and, when it becomes stationary, take several readings. Take the average of the temperatures and record it as the result of a determination of the melting-point of ice.

Suppose you had placed liquid water in the beaker; had surrounded the beaker with a freezing mixture and taken the temperature when the water was partially frozen, would the result have been the same?

What evidence have we that ice and water are two forms of the same substance?

Make a mixture of salt and crushed ice and take the temperature as before. (?)

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[1] c.c. will be used hereafter as the abbreviation for cubic centimeters. 100 c.c. is about one-half the capacity of a kitchen cup.

EXPERIMENT 6.—Half fill a small beaker with distilled water, dry it on the outside and support it on wire gauze. Clamp a thermometer so that the bulb is in the liquid and heat. Watch the thermometer. Small bubbles escape before the liquid begins to boil. Explain this. What would be the effect of putting fish in water which had been boiled and then cooled in the absence of air?

When the liquid boils, take several readings of the temperature. Record the results. What is the effect of variation of pressure on the boiling-point of water. Why is it difficult to cook certain kinds of food on high mountain-tops?

With a pipette measure off 50 c.c. of water into a 100 c.c. beaker. Dissolve in the water 10 grams of salt and take the boiling-point of the solution. Repeat, using 10 grams of sugar. How do the boiling-points of solutions of solids compare with that of pure water? Does sugar or salt more strongly affect the boiling-point?
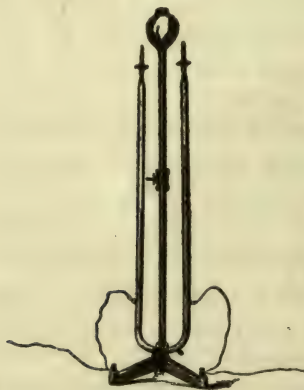
EXPERIMENT 7. — Carry out the *electrolysis of water* in the apparatus shown in Fig. 6. Dilute some sulphuric acid with about ten times its volume of water. *In diluting sulphuric acid pour the acid into the water in a thin stream, stirring constantly—never the water*

FIG. 6.

into the acid. (With the other acids it is a matter of indifference.) Cool this liquid by standing it in a tin pan full of water. Fill the apparatus with the liquid by pouring it into the funnel tube until it just reaches the stopcocks. The latter must be open during this operation.

Close them and connect the two pieces of platinum foil in the apparatus with a battery or a dynamo-circuit. Allow the current to pass until about 15 c.c. of the gas which is formed in smaller quantity has collected. Do not let the level of the liquid fall as far as the platinum foil.

Stop the current, and if the apparatus is graduated, read off carefully the volumes of both gases. *Read from the bottom of the meniscus* (Fig. 7). If the apparatus is not graduated, measure the length of each gas-column with a meter scale. What is their relation by volume?

Cautiously open each stop-cock for an instant to drive out any water which may be above them. Obtain a pine splint bearing a spark by extinguishing the flame of the burning splint by a quick movement of the hand. Let the gas which is present in smaller quantity stream out against
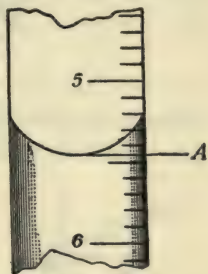
FIG. 7.

the spark. (?) Slip over the end of the other tube a very short piece of rubber tubing connected with a short piece of glass tubing drawn out to a fine jet. Let the gas escape against the flame of a burning match, and remove the flame. (?) What evidence does this experiment furnish of the composition of water? Why does the level of the liquid in the apparatus sink so slowly when it is run with the stop-cocks open, although much gas escapes? What becomes of the sulphuric acid and what is the object of adding it? (Part I, p. 6).

EXPERIMENT 8.—**Qualitative synthesis of water.**—Fill a U-shaped tube with fragments of dry calcium chloride, free from powder. Cork the open ends of the tube tightly and connect it on the one side with a Kipp generator furnishing a current of hydrogen, and on the other with a

short tube of hard glass drawn out to a jet (Fig. 8). Pass a gentle current of hydrogen through the tube for a few
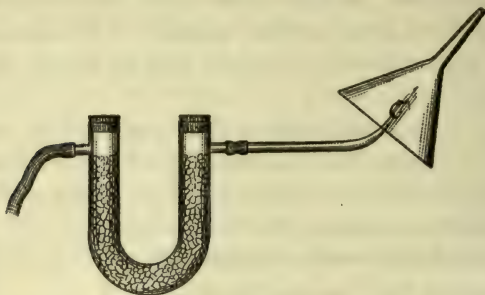
Fig. 8.

seconds to drive out the air, and then light the gas at the jet. Hold over the flame a cold, dry funnel. (?) What is the conclusion? Make a drawing of the apparatus. The object of the calcium chloride is to dry the gas. Why? Hold a cold, dry cylinder or bottle over a burning candle for a moment. Over a small gas flame. (?) What evidence does this furnish with respect to the composition of the gas and the candle?
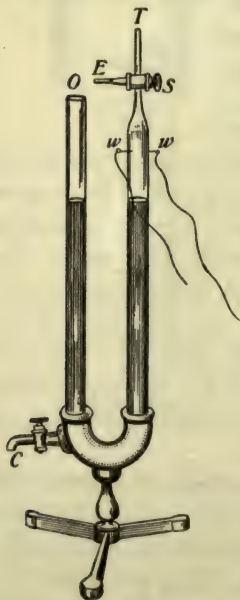
EXPERIMENT 9.—**Quantitative synthesis of water.**[1]—This experiment is made in the U-shaped eudiometer (Fig. 9). The end at O is open. The other limb of the

Fig. 9.

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[1] This experiment requires some expertness in manipulation. It will be well to carry it out on the lecture-table at this stage, or to postpone it until the student has acquired some skill in the handling of apparatus.

U is closed by a three-way stop-cock *S*. This stop-cock is so constructed that gas passed in through *T* will either escape into the air by the stem *E* or pass down into the eudiometer, according to the position of the stop-cock. Take out the stop-cock and inspect it until you understand why this should be the case. If necessary smear a *little* vaseline thinly over it, put it back in place and turn it until the vaseline is evenly distributed. This will make it air-tight, which is essential to the success of the experiment.

Open *S* and close the stop-cock at *C*. Pour mercury in at *O* until the apparatus is filled to the level of *E*, but not above it.

Fit a test-tube with a perforated cork and delivery tube (Fig. 10). Over the end of the delivery tube slip a short piece of rubber tubing which will readily slip over the stem *T*, making an air-tight junction. Fill this test-tube to the depth of 2 cm. ($\frac{4}{5}$ inch) with a mixture of 1 part manganese dioxide and 3 parts potassium chlorate. Heat very gently, proceeding exactly as directed in Experiment 23. From time to time test the gas given off through the delivery tube with a splint bearing a spark. When the spark bursts into flame, adjust the three-way stop-cock of the eudiometer so that gas admitted

FIG. 10.

at *T* will escape at *E*, and let oxygen stream through the tip and stop-cock for ten or fifteen seconds. (Why?) Then turn the stop-cock so that the oxygen passes into the tube over the mercury and allow 5 to 8 c.c. of oxygen to pass in. Turn the stop-cock so that the oxygen in the eudiometer is shut off both from the external air and from the oxygen-generator, and *at once* remove the latter.

Place a dry beaker under the stop-cock *C*, and allow mercury to run out until the level of the mercury in the two limbs is the same.[1]   (Why?)   Be careful in all these manipulations not to touch with the hands that part of the tube containing the oxygen.   (Why?)   Read and record the volume of the oxygen.   Repeat the reading.

Now transfer your cork and delivery tube to another test-tube in which you have placed a few pieces of granulated zinc, about 3 cm. (1 inch) of water over them and enough sulphuric acid—added very gradually—to produce a rather brisk evolution of hydrogen.[2]   Turn the stop-cock so that gas passed in at *T* will escape at *E*. *Be careful in doing this not to throw the oxygen into communication with the air, as this would spoil the experiment.*

Slip the rubber tube over *T* and allow the hydrogen to stream out through *E* for about two minutes.   (Why?) Pass about three times as much hydrogen as you have taken of oxygen into the eudiometer, turn the stop-cock so as to shut it off from the air and the hydrogen generator, and remove the latter.   Equalize the levels of the mercury in the two limbs, read off the volume of hydrogen added, and let the apparatus stand several minutes to give the two gases time to mix thoroughly.

The two gases can now be caused to combine by a spark passed between the platinum wires *w w*.   The spark can be obtained from an induction coil excited by three Edison-Lalande or by two dichromate cells.   Since the explosion may possibly be violent enough to wreck the apparatus, it is well to take the precaution of running out mercury at *C* until the level of the mercury in that limb

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[1] If by mistake too much mercury is run out, add mercury at *O* until the level is higher in that limb, and again run out through *C* until the levels are the same.

[2] The hydrogen is best taken from a Kipp apparatus if one is at hand.

is much lower than in the other. This dilutes the gases and reduces the violence of the explosion. Before passing the spark, put the thumb tightly over O to prevent any mercury being thrown out.

Let the apparatus stand for five minutes, equalize the levels of the two mercury-columns and read off the volume remaining. Record it. Pour mercury into O and show that the residual gas is hydrogen by letting it escape at T and burning it. Slip a short rubber tube bearing a jet over T before doing this, otherwise the heat of the flame would crack the apparatus. Make the calculation as in the following example:

Suppose you have taken.............. 7 c.c. oxygen, and that the volume after adding hydrogen is 27 c.c.;

then the volume of hydrogen added is.... 20 c.c.

Suppose further that the volume after the explosion is 6.1 c.c.

This residual gas is shown by investigation to be hydrogen. It is clear that 20 — 6.1 or 13.9 c.c. of hydrogen must have disappeared with the 7 c.c. of oxygen, to form water. Hence the relation by volume in which the gases combine is 7 : 13.9 or 1 : 1.98.

Make a drawing of the apparatus in your note-book and give a complete description of your work. Explain the calculation. What becomes of the water formed in the explosion and why is its volume not considered? Is the composition of water always the same? If so, how do you account for the fact that different experiments, even when carried out with great care, always yield slightly different results?

The more numerous and careful the experiments the more closely the average result of them will approach the ratio 1 : 2.

What general statement can be made about the volumes in all cases in which two gases combine?

How can you calculate the composition of water by weight from its composition by volume?

EXPERIMENT 10.—**Action of oxygen on copper. Synthesis of water from hydrogen and copper oxide.**—Fit up the apparatus shown in Fig. 11. $T T'$ is a piece of hard
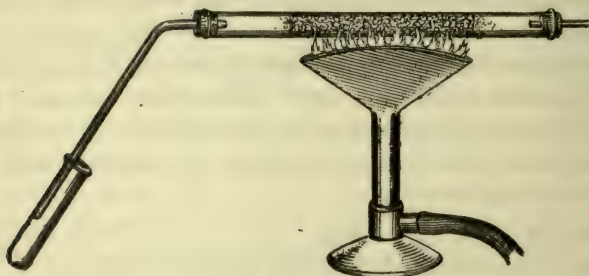
FIG. 11.

glass tubing, 1 cm. or more in diameter and about 30 cm. (1 foot) long. In order to cut off a suitable piece of tubing, first make a notch on the tube at the point where it is desired to cut it. Then wrap several layers of wet filter paper around the tube quite close to the notch, and do this also on the other side of the notch (Fig. 12), so that

FIG. 12.

a narrow band of glass, 1 cm. wide or less, with the notch is left bare. If this bare portion is held in the burner flame, it will usually break off evenly, and any projecting portions can be removed by careful chipping with a key.

Thrust a loose plug of asbestos into the tube about 5 cm. (2 inches) from one end, and upon this pour a column of copper clippings about 20 cm. (8 inches) long. Put a similar loose plug of asbestos in the other end of the tube to hold the clippings in place. Holding the tube horizontal, tap it gently upon the table so as to cause the

clippings to settle, and make a channel for the passage of gases.

Select two corks a trifle too large to fit in the ends of the tube, and roll them carefully under the foot until they fit. Perforate the corks either with a rat-tail file or a cork-borer, and fit them with tubes, as in the cut. In perforating with a rat-tail file, thrust the sharp end of the file through the middle of the cork, beginning with the small end, and resting the cork on the table. Then enlarge the hole with the rough part of the file until the glass tube fits it *tightly*. The glass tubes must be rounded at the ends, and must be introduced with a twisting motion and without strong pressure, the use of which is likely to break the tube and seriously cut the hand.

Clamp the tube, or suspend it by a wire, and apply heat from a wing-top burner, very gently at first. If clamps are used, they must be placed at the ends, so as not to be burned. Raise the temperature gradually until the copper is at a dull red-heat. If the tube softens or shows signs of bending, moderate the heat.

Now connect the short straight glass tube with a test-tube in which oxygen is being generated from potassium chlorate and manganese dioxide (Experiment 23), and pass oxygen through it. What is the result? Describe the product. What is its composition? At which end of the tube does the change begin, and why?

Remove the oxygen generator and connect the tube with a hydrogen generator. The Kipp apparatus is best. *If an ordinary generator is used, hydrogen must be allowed to escape briskly from the exit tube for at least five minutes before connecting it to the red-hot tube.* The hydrogen must be passed through a U-shaped tube containing dry calcium chloride in lumps—not powder—to free it from water before it enters the copper tube. See Experiment 22 for the method of generating hydrogen.

What change takes place in the black substance? Hydrogen has a similar effect on the compounds of oxygen with many metals—for instance, upon tin oxide and lead oxide. The effect is called *reduction*. Some other oxides, like those of magnesium and aluminium, are not affected by it.

Look in the cooler part of the tube, and in the bent tube, for evidence of the formation of *water*. What evidence of the composition of water is furnished by this experiment?

PROBLEMS

1. The electric current is passed through water containing sulphuric acid until 20 grams of the water have disappeared. What weights of hydrogen and of oxygen have been liberated?

2. 300 grams of water are decomposed. What weights of hydrogen and oxygen are produced?

3. If 27.396 grams of water contain 24.352 grams of oxygen, what is the percentage composition of water?

4. A quantity of hydrogen gas weighing 4 grams is slowly passed through a glass tube containing a large quantity of copper oxide heated to redness. (*a*) How much will this tube lose in weight? (*b*) What weight of water will be produced?

5. 50 c.c. of hydrogen are mixed with 50 c.c. of oxygen and the mixture exploded. (*a*) If the process takes place below 100°, which gas remains in the tube, and how much? (*b*) If the whole process takes place above 100°, what is the total volume remaining in the tube, and of what does it consist?

CHAPTER II

SOLUTION

EXPERIMENT 11.—**Soluble and insoluble.**—Place a little coarsely powdered rosin in a test-tube, cover it with water, and shake it. (?) Pour out the water, cover the rosin with alcohol, and shake. (?) Reserve this liquid.

Shake up some copper sulphate, first with alcohol, and then with water. (?) Give definitions of the terms soluble, insoluble, and solution.

Pour the alcoholic solution of rosin into a large quantity of water in a bottle or cylinder. (?) The resulting state of things is called *a suspension.* State some differences between solutions and suspensions.

EXPERIMENT 12.—**Saturated solutions.**—Half fill a liter flask with water and add small quantities of salt, shaking after each addition until the liquid will dissolve no more. Cork the flask and shake the liquid containing a little undissolved salt for a long time, to make sure that it will not take up any more. Pour off the liquid into a narrow cylinder and take its density by means of a *hydrometer* (Fig. 13). Most solutions are denser than water. How about salt-solution? The density will serve as an indication of the amount dissolved. Of course if two solutions of table-salt have the same density, they contain the same percentage of dissolved salt.
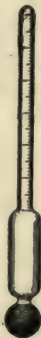
Fig. 13.

Half fill the flask again with water and add a large quantity of salt, several times as much as the water can dissolve. Shake for some time. The liquid should contain a sediment of undissolved salt more than 5 cm. in depth. Finally, let the liquid settle, pour off into a narrow cylinder, and take the density as before. The result should be the same.

This important experiment is an example of the fact that *the quantity of a substance which dissolves to produce a saturated solution does not depend upon the excess of undissolved solid present in the liquid.* There must be some solid present; otherwise the liquid would not be saturated; but a solution which remains in contact with a small quantity of a solid without dissolving any more of

it, is just as strong as one which is in contact with a large quantity.

EXPERIMENT 13.—**Effect of temperature on solubility. Crystallization.**—Powder some potassium chlorate in a mortar, not by pounding it, but by moving the pestle with a strong, steady pressure. Place 50 c.c. of water in a 100 c.c. beaker and add potassium chlorate to it in small quantities. Stir until each portion is dissolved before adding the next.

When the liquid is saturated, place the beaker on wire-gauze on a ring of your stand and heat it gently. Continue stirring and adding more potassium chlorate. What is the effect of temperature on solubility? Stand the beaker aside to cool. (?) What is the most obvious difference between a crystal and a bit of non-crystalline matter?

This is by no means the only difference. The great distinction is that all properties which *have direction at all,* are different in different directions in a crystal. Thus, a crystal breaks more easily in some directions than in others ; it conducts heat better in certain directions ; it transmits light quite differently along certain lines, and so on. Even the solubility of a solid is different on different faces of a crystal.

For all these reasons, if a crystal is broken into any irregular shape, it is easy, in spite of this, to identify it as a piece of crystalline matter ; while on the other hand, if a mass of glass is cut into the exact shape of a crystal, it is equally easy to show that it is a fragment of non-crystalline (amorphous) material artificially shaped.

Heat some clear lime-water to boiling in a test-tube. Take the lime-water out of the bottle with a glass tube, and avoid stirring up the material at the bottom. This applies only to lime-water. All ordinary liquids are to be poured carefully from the bottle, not withdrawn by means of tubes. Cork the lime-water bottle at once after using it, since the air spoils it. Does the liquid become

turbid? Does heat affect the solubility of lime in the same way as it does that of potassium chlorate? How do almost all solids behave in this respect?

EXPERIMENT 14.—**Supersaturated solutions.**—Place a few drops of water in a test-tube, half fill the tube with sodium thiosulphate—called "hypo" by the photographer —and heat with a small flame kept in constant motion. When complete solution has occurred, pour the liquid into a clean tube and cork it to exclude dust. Let it cool. Does it behave like potassium chlorate solution on cooling? Throw into the cold liquid a fragment of solid sodium thiosulphate. (?) What is a *supersaturated* solution? Do you regard it as a stable or an unstable state of things? Would *any* crystal answer the purpose, if dropped into the supersaturated solution in this experiment? Since a solution which does not contain any of the undissolved solid may be either unsaturated or supersaturated, what is the only way of being sure that a solution is *saturated?*

FIG. 14.

EXPERIMENT 15.—**Solutions of liquids in liquids.**—To a test-tube of water add a drop of chloroform. Cover the tube with the thumb and shake it. Are the liquids apparently insoluble in each other? Are they really insoluble in each other?

Half fill a small separatory funnel (Fig. 14) with water. Add a little ether, insert the stopper and shake. *Ether is highly inflammable, and must not be used in the neighborhood of a flame. The ether-bottle must be kept tightly corked.* Add another small quantity of ether and shake again. (?) Now add about half as much ether as there is water present, and shake. Is ether soluble in water? Is there a limit to its solubility? What is the composition of the two layers in the funnel? Give a suitable name to each layer. Allow about 30 c.c. of the lower layer to

run into a 100 c.c. beaker, and get rid of the remainder of the liquid by running it down the sink with an abundance of water. Place the beaker on wire gauze and, having first made sure that no one in the neighborhood is working with ether, heat it gently. Hold a lighted match over the beaker. (?) Did the lower layer contain ether? Is the solubility of ether in water increased or decreased by heating? The solubility of water in ether is increased by heat.

Fill a test-tube one-fourth with alcohol and add water in small quantities, shaking after each addition until the tube is full. What is the result? Is it possible to obtain two layers by mixing alcohol and water? Some other pairs of liquids—for instance, alcohol and ether—behave in the same way.

EXPERIMENT 16.—**Solutions of gases in liquids.**—Heat some faucet water in a beaker on wire gauze not quite to boiling. (?) Heat some ammonia water in a beaker. Hold a burner flame over the beaker. Is there any evidence that a gas escapes? What is the effect of rising temperature on the solubility of a gas?

Fill a 100 c.c. beaker with soda-water from a siphon bottle. What is soda-water? What was the cause of the effervescence when the liquid escaped into the beaker? How does the solubility of a gas vary with the pressure? Lower into the liquid a sealed tube, open end down. Throw into it a fragment of charcoal. Explain the results.

Taste some of the soda-water. Place about 10 c.c. of it in a test-tube and boil it for a time. Cool by running water over the tube and taste again. Is the taste the same? Why? What is the cause of the unpleasant taste of boiled water, and how can it be remedied?

PROBLEMS

6. 10.98 grams of a solution of potassium chlorate saturated at 18° was placed in a weighed dish and evaporated to dryness. The residue weighed .7025 gram. How much potassium chlorate was contained in 100 parts of the solution ?

7. Taking the figures stated in problem 6, how much potassium chlorate will 100 parts of water at 18° dissolve ?

8. Taking the same figures, how much water at 18° is necessary to dissolve 1 gram of potassium chlorate ?

9. A solution of common salt saturated at 15° contained 26.39 per cent of salt. How much salt will 100 grams of water dissolve at 15° ?

CHAPTER III

PHYSICAL AND CHEMICAL CHANGE—LAW OF THE INDESTRUCTIBILITY OF MATTER

EXPERIMENT 17.—**Changes in matter.**—Take a piece of platinum foil in forceps and hold in the Bunsen flame. Let it cool. (?)

Tear up a little paper in very small pieces and bring near it a roll of sulphur. Rub the sulphur briskly on the coat-sleeve and again bring it near the paper. (?)

Crease a long narrow piece of paper in the middle so as to make a trough, which will slip into a test-tube. By means of this introduce a little *mercuric iodide* into a clean, dry test-tube, without getting any of it on the sides. In doing this hold the tube horizontally and slip it over the paper, near the end of which the mercuric iodide is placed. Then upset the trough and deposit the mercuric iodide in the bottom of the tube. Always use this method of introducing powders into tubes when you desire to keep the upper portion of the latter clean.

Lay a cork loosely in the mouth of the tube and weigh

it or balance it with copper filings or iron filings. Before weighing be sure that it is absolutely clean and dry on the outside, and all through the experiment handle the tube with paper—not with the fingers—to avoid soiling it.

Now heat the tube very gently. It should be simply brushed with the flame once in two or three seconds and the powder should be constantly shaken about. The temperature must not rise much above the boiling-point of water. *Overheating will melt the mercuric iodide and spoil the result.*

When the change is complete stop heating, let the tube cool, and weigh it again. Is the weight the same? What does the result show? What is the substance in the tube? Throw out half of it on a piece of paper and rub it with a glass rod. (?) Let the rest of it stand over night and examine it in the morning. (?) What is the natural state of mercuric iodide at ordinary temperatures? At slightly elevated temperatures? In what respects does this change resemble and in what respects differ from the transformation of water into ice? In what respect do all the changes carried out in Experiment 17 resemble each other? Mention some other changes in matter which are like them in this respect.

Experiment 18.—**Changes in matter. The law of the indestructibility of matter.**—Take a short piece of magnesium ribbon in forceps and hold one end of it in the flame. Receive the product in a dish and examine it. It is called *magnesium oxide*. Why? Compare this change with the heating of platinum.

Place in a small hard glass test-tube enough *mercuric oxide* to fill it to the depth of 1 cm. or more. Introduce the powder by means of a paper trough. Clamp the tube horizontally, placing the clamp near the mouth so that heat can be applied without spoiling the clamp, and heat gently, brushing the tube with a small flame. Hard-glass

tubes must be heated with great caution, for they break very readily. When the mercuric oxide changes color, examine it and let the tube cool. What kind of a change is this? When mercuric acid is cooled to —200° C. it becomes sulphur-yellow, and resumes its original tint on being allowed to warm to room temperature.

Fit the test-tube with a perforated cork bearing a delivery tube, and arrange the apparatus as shown in Fig. 15. Apply heat, at first very gently, gradually raising the
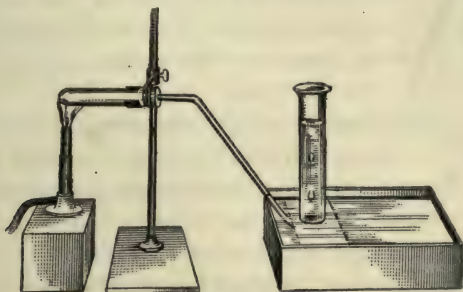
Fig. 15.

temperature to redness. Collect two test-tubes and a small cylinder of the gas given off. Apply the yellow flame of the burner and cover the hot tube with a layer of soot to make it cool gradually and avoid cracking. Disconnect the apparatus. Examine the residue in the tube. What is it? Record the properties of the gas collected. Into a test-tube of it introduce a spark. (?) Slip a glass plate under the cylinder full of the gas and place it upright on the desk. Draw aside the plate for an instant and introduce into the gas a piece of burning candle, held erect on a bent piece of stiff wire. (?) What is the gas? *Keep the flame out of contact with the glass.*

Sketch the apparatus in your note-book and write a full description of your work. What is the historical interest of this experiment? Clean the hard-glass tube when

perfectly cold by washing it out thoroughly with water, then allowing a little strong nitric acid to remain in it for a time and finally washing with water again.

Weigh roughly about 1 gram of potassium iodide and dissolve it in a small test-tube about half full of water. Weigh roughly 0.7 gram of mercuric chloride and dissolve it in about 100 c.c. of water in an Erlenmyer flask. *Mercuric chloride is very corrosive and poisonous, and must not be touched with the fingers. If any of it gets upon the hands it must be removed at once by washing with water.* Carefully place the test-tube in the flask. Remember that chemical glassware is purposely made thin and will not endure violent treatment.

FIG. 16.

Hold the flask upright, see that it is absolutely dry and clean on the outside, and cork it tightly. The completed apparatus is shown in Fig. 16.

Now take hold of the flask by means of a folded paper and place it on the trip-scales or a large lecture-table balance. Weigh it accurately, or balance it by metal filings. Record the weight, or leave the filings on the balance; take the flask with the paper holder and tilt it so that the liquids mix. What happens? The red substance is mercuric iodide. This accounts for the mercury and the iodine, but there must be another compound produced. Of what two elements? What becomes of this compound? Devise a method of obtaining it.

Put the flask back on the balance and weigh it again. How do the weights compare? What law have you exemplified? State the law in several different ways. Why is it important? What evidence does astronomy furnish of its truth?

CHAPTER IV

MIXTURE—ELEMENT—COMPOUND—THE LAW OF DEFINITE PROPORTIONS

EXPERIMENT 19.—**Mixtures and compounds.**—Powder finely some roll sulphur (about 3 grams) and mix most of it with about an equal weight of iron filings. Reserve a little. Examine a little of the mixture with a lens. Can you perceive iron and sulphur in it? Place a little of the mixture in a beaker half full of water and stir it. (?) Devise a method of separating the two based upon this behavior.

Place a little iron filings in one dry test-tube, and a little powdered roll sulphur in another, and try the behavior of both with a few drops of *carbon disulphide.* Which dissolves?

Carbon disulphide is inflammable and must not be used in the vicinity of flame. The bottle must be kept corked. The vapor is injurious and should be inhaled as little as possible.

Now place a little of the mixture of iron and sulphur in a dry test-tube, and shake it up with about 5 c.c. of carbon disulphide. Allow to settle, and pour off the clear liquid into a dry dish. What is the substance in the test-tube? What remains in the dish after the carbon disulphide has evaporated?

Place a small portion of the mixture of iron and sulphur on a piece of paper and stir it with a magnet. Explain.

Now transfer the rest of the mixture to a dry test-tube, tap the tube on the table to make a channel along the upper surface, clamp the tube horizontally near the mouth and apply a burner flame to the extreme bottom. It is well to place a tin pan under the tube in case of breakage.

Here, and in all such cases, do not keep the hand directly under the tube while heating. When the reaction begins, remove the flame and observe. Is energy evolved or absorbed when iron and sulphur combine? Let the tube cool, break it, if necessary, and examine the product. It is a chemical compound of iron and sulphur, called *iron sulphide.* Powder it, and examine some of it with a lens. Are iron and sulphur visible in it? Will carbon disulphide extract the sulphur from it?

Explain all the distinctions between a compound and a mixture which are exemplified in this experiment. Notice that all these differences are the result of the fact that the mixture is composed of *two* substances, each having its own properties, while the compound is *one* substance.

However, the greatest distinction between compounds and mixtures does not appear at all in this experiment. What is it?

The exact quantities in which iron and sulphur combine to form iron sulphide is 56 parts of iron to 32 parts of sulphur. Clearly we took more sulphur than was necessary. What became of it? What would have been left in the test-tube if we had taken more iron than was required for the sulphur?

EXPERIMENT 20.—**The law of definite proportions.**—Clean and dry a porcelain crucible carefully and weigh it with the cover. Record the weight. Count the weights at least twice, once while they are upon the pan of the balance and once upon returning them to the box, to be sure there is no mistake. Handle the weights with forceps. They must not be touched with the fingers. Be sure that both pans of the balance are *clean* before weighing.

Introduce into the crucible from 0.3 to 0.5 of a gram of powdered magnesium and weigh again accurately. Be sure that none of the magnesium is upon the balance pans,

since this will make all your work useless. Again count the weights at least twice.

Support the covered crucible on a pipe-stem triangle on a ring of the stand and allow a Bunsen flame to touch the bottom. After ten minutes place the cover so as to allow a very limited access of air. *The operation must be so conducted that nothing escapes from the crucible.* If any white smoke (magnesium oxide) should appear, the crucible must be covered at once. After ten minutes more, lift the cover by the ring with the forceps and shake into the crucible any magnesium oxide which may adhere to it, turn up the flame until it half covers the open crucible, and heat strongly for five minutes, turn down the flame gradually, extinguish it, cover the crucible, let cool five minutes, and weigh. The magnesium oxide in the crucible should be white or grayish-white.

The following will serve as an example of the proper method of record and calculation:

Weight crucible, cover, and magnesium........... 15.06
  "   "   and cover, empty................ 14.64

    Magnesium taken .... .42

Weight crucible, cover, and magnesium oxide...... 15.34
  "   "   "   and magnesium........... 15.06

    Oxygen taken from air.................... .28

Therefore, 0.42 gram of magnesium combines with 0.28 gram of oxygen. Calculate the oxygen which will combine with 1 gram of magnesium, thus:

$$.42 : .28 = 1 : x.$$
$$x = \tfrac{2}{3} \text{ gram, or } .66.$$

Calculate also the quantity of magnesium which would combine with 1 gram of oxygen, thus:

$$.28 : .42 = 1 : x.$$
$$x = 1.5 \text{ grams.}$$

Calculate in the same way the quantity of oxygen which would combine with 24 grams of magnesium and the quantity of magnesium which would combine with 16 grams of oxygen.

If time permits, repeat the entire experiment. If not, compare your results with those of others who have done the same work. If the experiment is properly performed, different results should be nearly the same. (Why not exactly the same?) If your result varies widely from the figures given above, first look for errors in the calculation, and if none are found, repeat the experiment.

Does the same weight of magnesium always combine with the same weight of oxygen? Is the composition of magnesium oxide always the same? How about other compounds? State the law. What bearing have the results obtained in the electrolysis and synthesis of water upon the law? Explain exactly what is meant by the statement that magnesium and oxygen are elements and magnesium oxide a compound of them. Why are solutions *mixtures* although they are homogeneous and can not be separated by mechanical methods?

CHAPTER V

HYDROGEN

EXPERIMENT 21.—**Reaction of sodium and water.**— *Sodium must not be touched with fingers which are in the least moist either with water or perspiration. Your desk must be dry when working with it and everything with which you touch it must be scrupulously dry. The air acts rapidly upon sodium and it must not be exposed. Take only a small piece from the bottle at a time, and imme-*

diately cork the latter. The liquid over the sodium in the bottle is naphtha or kerosene, and the bottle must not be opened in the vicinity of a flame. No sodium must be put away under the desk or allowed to remain lying about, since it may catch fire. None must be thrown into the waste-jar, since it may ignite the paper or other substances which the jar contains. Return any unused portions to the bottle, or place in a vessel specially provided for that purpose.

Throw a clean piece of sodium, free from crust, half the size of a pea—*no larger*—into a cylinder half full of water. Immediately cover the cylinder with a glass plate or a piece of paper, and *wait until the reaction is over before removing the cover.* The action usually ends with a slight explosion which may endanger the eyes if the cover is removed too soon.

Describe what happens. Throw in another similar piece of sodium. Feel the water of the cylinder between the fingers. (?) Taste a little of it. (?) *Here, and always, immediately reject the liquid tasted and rinse out the mouth with water. Do not taste substances unless directed.* Try the behavior of the liquid with red and blue litmus paper, pieces about 1 cm. square or less. (?) Allow to fall into the liquid a drop of a solution of phenol phthalein. (?) What are these new properties of the liquid due to?

Wrap a clean piece of sodium half the size of a pea in dry tea-lead (lead foil). Punch several holes in the lead with a knife-blade. Invert a test-tube full of water in a tin pan containing water, and quickly slip the lead containing the sodium under it. If necessary use another smaller piece of sodium wrapped in lead to complete the filling of the tube. *Take no more sodium than is directed.* The use of larger quantities is likely to cause explosions which may imperil the sight.

What gas collects in the tube? Does it come from the water or the sodium? Has the gas any color or odor? Is it soluble in water? Does it burn? Quietly or with explosion? To what product?

Record exactly what you observe. For instance, if you find the gas has an odor, record it, and if you think the fact peculiar, inquire of the instructor. *Never alter your observations to correspond to preconceived notions.*

EXPERIMENT 22.—**Hydrogen from zinc and sulphuric acid.**—Place about 20 grams of granulated zinc in a gas-generating bottle. The bottle must be held almost horizontal and the zinc allowed to slide into it, otherwise the shock of the falling zinc will break it. The bottle is provided with a doubly perforated cork carrying a funnel tube and a delivery tube, and the apparatus is arranged for collecting the gas over water (Fig. 10, Part I).

Insert the cork tightly with a twisting motion, and pour in through the funnel tube enough water to cover the zinc thoroughly. The funnel tube must dip into this water. Extinguish any burner flame that may be in the neighborhood, and slowly add strong sulphuric acid through the funnel tube until gas is briskly evolved. Do not add too much acid. The maximum should be about one-fourth as much by volume as there is water present. Allow the gas to escape through the water for three minutes. Why? *Do not attempt at any time in the experiment to light the gas at the exit tube.*

Collect the gas over water in wide-mouthed bottles of about 300 c.c. capacity. Determine its properties. Has it any color or odor? Is it soluble in water? Does the method of collecting it throw any light on this last question? In order to obtain more definite information fill a test-tube half full of hydrogen and mark the level of the water by a s i of gummed label on the tube. Then shake the tube for a time, keeping its mouth under

water. (?) Use this method hereafter in testing the solubility of gases.

Will the gas burn? Try a bottle of it—*not the exit tube of the generator.* Will it support combustion? Try it by holding a bottle-full mouth downward and introducing a lighted candle fastened on a wire. Keep the candle out of contact with the walls of the cylinder so as not to wet the wick. Withdraw the candle slowly. (?) Repeat.

Fill two bottles of the same size with the gas. Support one in an inverted position in a ring of your stand, the mouth not touching the table. Place the other upright. Uncover them at the same moment and allow both to remain uncovered for two minutes. Now thrust a lighted taper or match into each in turn. Draw conclusions.

Fill a small strong bottle over water $\frac{4}{5}$ with air and $\frac{1}{5}$ with hydrogen. Ignite the mixture. Explain the cause of this behavior? Why does not the flame strike back from gas-jets along the mains to the gas-works? Would it be safe to supply cities with a mixture of gas and air by means of pipes?

Procure a strong round-bottomed ginger-ale bottle and a cork which will fit it. Perforate the cork so that an artificial straw like those used at soda-fountains will fit fairly well in the hole. Put in the bottle some granulated zinc and water and add enough sulphuric acid to produce effervescence. Immediately insert the cork bearing the straw and light the end of the straw, holding the bottle upright, and the face *away from over it.* What is the cause of the explosion? Would an explosion have occurred if you had waited several minutes before lighting the straw? Why is it dangerous to light the hydrogen at the exit tube of your generator? *Whenever it is necessary to do this you should wrap the generator, cork, and funnel-tube carefully with a towel, so that no harm can*

result, and wait five minutes before applying the light.
This applies not only to hydrogen but to all combustible
gases.

Filter the liquid which remains in your gas-generating
bottle into a clean porcelain dish. Prepare the filter by
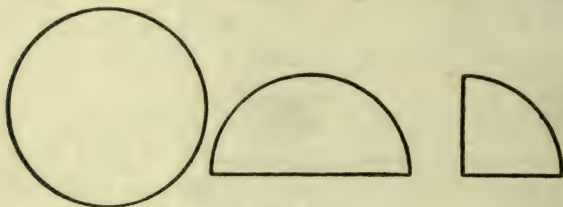
Fig. 17.

folding it first into a semicircle, then into a quadrant
(Fig. 17). Thrust it tightly into a funnel and wet it
to keep it in place. Support the funnel with its stem
against the side of the
dish, so that the liquid
will slip down the side
of the dish and not
splash. Pour the liq-
uid into the filter by
means of a glass rod
to avoid splashing
(Fig. 18). Never fill
up quite to the edge
of the filter, but keep
the latter nearly full,
as this makes the
process more rapid.
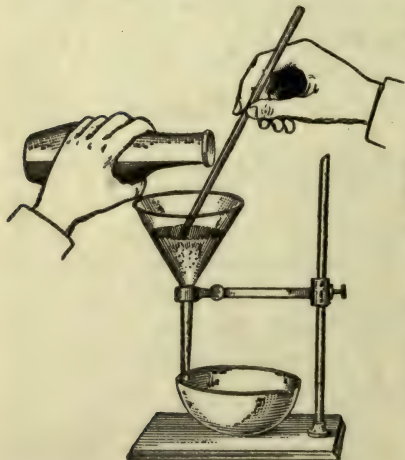
When the liquid
has all run through

Fig. 18.

wash off the zinc in the bottle, and return it to the stock
bottle of granulated zinc. Evaporate the liquid in the dish
down to one-fourth its bulk. No wire gauze is needed in

heating the dish. *The flame must not be allowed to touch that portion of the dish which is above the level of the liquid in it, and the dish must be dry on the outside.* The last sentence applies to all heating of liquids in vessels of glass or porcelain. Reduce the size of the flame as the liquid becomes less.

When only one-fourth of the liquid remains, let it cool. If nothing happens on cooling, evaporate carefully one-half of the remaining liquid and allow to cool again. Describe in your notes the crystals which separate. They are called *zinc sulphate,* and they contain zinc, sulphur, and oxygen. Sulphuric acid contains hydrogen, sulphur, and oxygen, so that we may describe the change which takes place in the gas-generating bottle by the statement that the zinc takes the place of the hydrogen.

CHAPTER VI

OXYGEN AND HYDROGEN PEROXIDE

EXPERIMENT 23.—**Preparation and properties of oxygen.**—Place about a gram of potassium chlorate—free from dirt—in a clean, dry test-tube and apply a gentle heat. At first the tube must be simply brushed with the flame. Notice the *decrepitation* and melting of the salt. Apply the spark test. (?) When no more gas escapes examine the residue in the tube. It is potassium *chloride.* Compare its taste with that of potassium chlorate. Heat some of it in a small tube of hard glass, sealed at one end. Does it give off oxygen? Does it melt as readily as potassium chlorate?

In a dry, clean test-tube melt carefully about a gram of potassium chlorate, remove from the flame and show that oxygen is not escaping by the spark. Now throw into

the tube about $\frac{1}{2}$ gram of powdered manganese dioxide and test again with the spark. (?) What is *catalytic action?*

Make a mixture of two parts of potassium chlorate and one part of manganese dioxide, by weight. Both substances should be *coarsely* powdered and *free from dirt.* Fill a wide test-tube to the depth of about 6 cm. with this mixture, make a channel by tapping on the table, and clamp the tube horizontally near the mouth. Provide a well-fitting cork with a delivery tube to collect the gas over water. Brush the tube with the flame. *Rapid heating or the presence of dirt in materials or tube may cause dangerous explosions.* When the gas begins to escape rapidly, remove the flame, and do not begin heating again until the evolution of gas slackens or ceases. Only a very moderate heat is required. A high temperature will melt the tube and spoil the experiment.

Collect the gas in wide-mouthed bottles. Let them remain with mouths under water until wanted, or, if there is not room for this, cover them with wet filter-paper plastered tightly over the mouth. Also collect half a test-tube full of the gas to investigate its solubility in the same way as with hydrogen. If the oxygen supply fails, remove the exhausted material in the test-tube by poking it with the handle of a spoon, put in fresh material and again heat gently. Record the properties of the gas, including its color, odor, and solubility. The cloudiness which it shows at first is due to dust carried over from the test-tube and will disappear on standing. Inhale a little of the gas.

Heat a piece of charcoal in a deflagrating spoon until it glows at one point. Remove it from the flame and plunge it into a bottle of oxygen. (?) Cover the jar with a glass plate and put it aside. Take another piece of charcoal and burn it in a bottle of air in a similar way. It may be necessary to heat the charcoal several times. Cover this bottle also. Examine both bottles. What is

evidently the nature of the product of the burning of char-coal? Into both bottles pour a little lime-water and shake. (?) Cloudiness produced in lime-water is evidence of the presence of *carbon dioxide* (so-called carbonic-acid gas). Does charcoal produce the same substance when it burns in oxygen as when it burns in air? Does it produce the same amount of heat? Why is the burning in oxygen more rapid and brilliant?

Put some sulphur in your spoon and start it burning in the air. Place the burning sulphur in a covered bottle containing air and allow it to burn for a time. Cover the jar and stand it aside. Place the burning sulphur in a bottle of oxygen. (?) Compare the two bottles. What is the nature of the combustion-product of sulphur? No-tice *carefully* the odor of the contents of each bottle. The odor is extremely irritating and suffocating. Shake up a little water in each, and add to the water a small piece of red and a small piece of blue litmus paper. (?) Heat the spoon red-hot to remove the sulphur and allow it to cool perfectly before using it again or putting it away.

Straighten a watch-spring by pulling it out into a line and drawing it slowly through the Bunsen flame. Slip aside the cover of a bottle of oxygen an instant and throw in a layer of sand 1 cm. deep. Cut a piece of match-stick 1 cm. long and split it for half its length. Slip this over the end of the watch-spring, set fire to it, and introduce it into a bottle of oxygen. The bottle must be kept covered during the experiment and the spring introduced between bottle and cover. If nothing happens, place another split match-stick on the spring and try again. What is the re-sult? Describe the iron oxide produced.

Put some magnesium powder in a small, clean, cold deflagrating spoon. The powder should project a little above the edge of the spoon. Start its combustion by let-ting the burner flame play upon it and let it burn in the

air. *Let cool,* and examine the magnesium oxide produced. It is dangerous to remove the substance until perfectly cold. Place some of it on a small piece of red litmus paper and wet it. After a minute remove the magnesium oxide. (?) Now fill the spoon again with magnesium powder, start it burning, and plunge it into a bottle of oxygen. (?) Examine this magnesium oxide and test it with red litmus paper as you did the other. Are the two identical?

Place a clean piece of sodium in your spoon—which must be cold and clean. Heat until the combustion starts and place in a bottle of oxygen, which must be kept covered during the experiment. After the combustion, introduce a little water into the bottle and shake. Test the liquid with red and blue litmus paper. Use very small pieces.

Sulphur is a non-metal. Notice that its oxide combines with water to produce a substance which turns litmus red—a substance which is an acid. Magnesium and sodium are metals. Their oxides combine with water to produce bases—substances which turn litmus blue. This is an important difference between metals and non-metals.

EXPERIMENT 24.—**Action of oxygen upon magnesium and iron.**—Cut a piece of asbestos board about 10 cm. square, and heat it for five minutes, to drive off moisture. Let it cool, place it upon the trip-scales or a lecture-table balance and place upon it a heap of magnesium powder about 2 cm. in diameter. Balance the other pan of the scales with small shot, copper filings or iron filings. Apply a burner flame to the tip of the heap. (?) Let cool and add shot or filings as required to restore equilibrium. Explain exactly what has occurred. Repeat the same experiment, using powdered iron in place of magnesium.

EXPERIMENT 25.—**Quantitative experiment. Decomposition of potassium chlorate. Weight of a liter of oxy-**

gen.—Before the student can make the calculations connected with the following experiment he must understand the methods of correcting the volumes of gases for temperature, pressure, and the presence of water vapor. Unless he has already taken up this subject in his course in physics, he should study the discussion in the Appendix and solve the problems there given. Fit up the apparatus shown in Fig. 19. *T* is a small hard-glass test-tube. *S* a tightly fitting stopper of red rubber, the tube from which just passes through the closely fitting rubber stopper of the acid bottle *A*. This bottle is filled with water
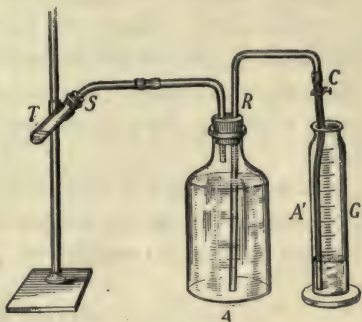
Fig. 19.

which has stood in the laboratory over-night, and is approximately at room temperature. *G* is a liter graduated cylinder. The tube *A A'* is filled with water by placing *A* in a beaker of water and sucking at *A'*. Then the Hoffmann clamp *C* is tightened and the stopper *R* tightly inserted, the tube *T* being removed. This tube is cleaned carefully, brushed with a flame until warm, and accurately weighed. Not more than 2.5 nor less than 1.5 grams of potassium chlorate is introduced into it, and it is brushed again with the flame until the potassium chlorate is just melted. *The heating must be stopped before any oxygen escapes.* Allow the tube to cool, and if any water has appeared in the upper portion, absorb it with a wisp of filter paper. Weigh the tube accurately. Find the quantity of potassium chlorate taken by subtraction.

Place the cold tube *tightly* on the stopper *S*, loosen the clamp *C* and cautiously heat the potassium chlorate, finally

to faint redness. *The secret of success is gradual heating.* Cool gradually, keeping the clamp *C* open and the rubber tube *A'* below the level of the water in *G*. Disconnect the apparatus. Take the temperature of the water in the bottle *A*, which is the same as that of the oxygen collected above it. Read the volume of the water in *G*, which is that of the oxygen (estimate to tenths of the divisions on the cylinder in doing this). Read the barometer in the laboratory, which will give you the atmospheric pressure under which the gas was collected. Repeat all readings to be sure there is no mistake. Record all readings at once in your note-book.

Weigh the tube *T* accurately and ascertain by subtraction the weight of the oxygen escaped from it. Also find by subtraction the weight of potassium chloride it contains.

Calculation

a. How much oxygen would 1 gram of potassium chlorate yield?

Solved thus:

$$\frac{\text{Weight oxygen escaped}}{\text{Weight potassium chlorate taken}} = x.$$

Has potassium chlorate always the same composition? Does your result agree fairly with those of others who have made the same experiment? Why not exactly?

b. What is the weight of 1 liter of oxygen just as you have collected it—that is, saturated with water and at the temperature and pressure of the air of the laboratory?

Solved thus:

$$\frac{\text{Weight oxygen escaped}}{\text{Volume oxygen in liters}} = x.$$

c. What is the weight of a liter of oxygen under standard conditions—that is dry, at a temperature of 0° and a pressure of 760 mm. of mercury?

Solved in the same way as c, but you must first find what the volume of your oxygen would be if dry and at 0° and 760 mm. This you can do, as explained in the Appendix (p. 150), by the formula:

$$V_o = \frac{V \times 273 \times P - w}{(273 + t) \times 760}$$

V_o = standard volume.

t = observed temperature at which your gas was measured.

P = observed pressure.

w = pressure of water vapor at the temperature t (this can be obtained from table in Appendix).

The following will serve as an example of the mode of calculating the results:

Volume of water collected in G...... 600 c.c., or .6 liter.
Temperature....................... 14° C.
Barometer......................... 756 mm.

The weight of the test-tube containing potas-
   sium chlorate, dried by being melted, was 12.50 grams.
Weight of empty test-tube................ 10.46

     Potassium chlorate taken............ 2.04 grams.

After being heated to redness the tube
   weighed............................. 11.70 grams.

Hence the weight of oxygen which escaped
was.................................. 12.50 grams.
                                       11.70 grams.
        Weight of escaped oxygen = .80 gram.

a. How much oxygen would 1 gram of potassium chlorate yield? Clearly the answer is equal to

$$\frac{\text{Weight of escaped oxygen}}{\text{Weight of potassium chlorate taken}} = \frac{.80}{2.04} = .39 \text{ gram.}$$

b. What is the weight of 1 liter of oxygen just as collected ?   The answer is given by

$$\frac{\text{Weight of oxygen}}{\text{Volume of oxygen}} = \frac{.80 \text{ gram}}{.6 \text{ liter}} = 1.33 \text{ grams.}$$

c. What is the weight of 1 liter of oxygen under standard conditions—that is, at 0° C., a pressure of 760 mm., and in perfectly dry condition?

First find the volume of your oxygen at standard conditions.   Use the formula

$$V_{\circ} = \frac{V \times 273 \times (P - w)}{(273 + t) \times 760}$$

$V = .6$ liter.
$t = 14°.$
$P = 756$ mm.

w (the pressure of water vapor at 14°) we find from table in Appendix = 11.9 mm.

Substituting these values,

$$V_{\circ} = \frac{600 \times 273 \times (756 - 11.9)}{287 \times 760} = 559 \text{ c.c., or } .559 \text{ liter.}$$

The weight of 1 liter of dry oxygen at 0° and 760 mm. would be

$$\frac{.80 \text{ gram}}{.559 \text{ liter}} = 1.43 \text{ grams.}$$

Do not expect your results to be identical with those given above.   The problem is simply to illustrate the method of calculation, and the numbers were chosen arbitrarily to give results quite close to the truth.

Very careful work has shown that
  the weight of a liter of dry oxy-
  gen at 0° and 760 mm. is....... 1.429 grams.
And that 1 gram of pure potassium
  chlorate gives off when heated.. .392 gram of oxygen.

Your results should not vary widely from these figures. If they do the experiment must be repeated; but before repeating it go over the calculation with great care, for the error is more likely to be found there than in the weights or measurements.

EXPERIMENT 26.—**Changes produced in air by respiration.**—Place some clean lime-water in a beaker, blow gently through it by means of a glass tube. (?) Invert three wide-mouthed bottles full of water in your tin pan and collect air in the first bottle from the beginning of an expiration. Withdraw the bottle from the water by means of a glass plate, slip the plate aside an instant and lower into the bottle a lighted candle. Does it burn as long as it would in the same volume of pure air? Why?

In the second bottle collect air from the end of an expiration, using the *last portions* of air from the lungs. Test this with a candle. (?) The result is due partly to the small amount of oxygen, and partly to the large amount of carbon dioxide.

Fill the lungs with air and hold the breath as long as you can without discomfort. Collect the first of the expiration and test it with a candle. Does the result furnish any evidence of the diffusion of carbon dioxide upward, or of oxygen downward, in the lungs?

The body burns up about 220 grams of carbon in twenty-four hours, almost all of which is cast out through the lungs as carbon dioxide. Weigh off roughly this amount of charcoal on the trip-scales in order to get an idea of the quantity. Of course the amount varies greatly in different people and in the same person at different times. The greater the activity and the lower the temperature of the surrounding air, the more active the internal combustion becomes.

EXPERIMENT 27.—**Ozone.**—Set up the apparatus illustrated in Fig. 16, Part I, and perform the experiment

described in the first part of paragraph 54. Make a sketch of your apparatus and write a description of your work. The oxygen required must be obtained from a cylinder of the compressed gas, *not made from potassium chlorate.* If there is no cylinder available, use air instead, but the proof is not conclusive. The induction coil can be excited by two dichromate or three Edison-Lalande cells, or in any other suitable way. Before beginning the experiment read the directions carefully, make a list of the things you need and procure them, so as not to be interrupted at a critical point by the lack of something essential. The solution of starch and potassium iodide must be *very dilute*—not more than 1 gram of starch and .2 gram of potassium iodide in 300 c.c. of water. It should be perfectly clear and limpid.

Procure an ozone tube (Fig. 16, Part I) and prepare ozone as described in paragraph 54, Part I. The apparatus is shown in Fig. 17, Part I. The current of oxygen comes from a cylinder or a gasometer and must be the *gentlest possible.* The slower the current the richer the gas will be in ozone, since it spends a longer time under the influence of the discharge. The preparation of pure ozone by intense cooling is too dangerous and difficult to attempt. Instead of this, note carefully the odor of the issuing gas and hold a piece of starch potassium iodide paper in it.

Place barium dioxide to the depth of about ½ cm. in a test-tube and allow some strong sulphuric acid to trickle down the side of the tube. Test the gas given off with starch potassium iodide paper and notice its odor. Cover the tube with a clean silver coin and stand it in a rack until the end of the laboratory period. If there is no apparent result, do not attribute the fact to an error in your work. The action requires a long time and a gas rich in ozone. Sketch the apparatus in your note-book.

What experimental evidence have you that ozone and oxygen are two forms of the same element? Which is the stable form of oxygen (1) at ordinary temperatures? (2) at slightly elevated temperatures (say 300°)? (3) at very high temperatures?

The existence of the same element in two or more different modifications is called *allotropy*. Do you know of any other elements which exist in *allotropic* modifications? Can you think of any allotropic modifications of carbon? Of tin? When the substance is a *compound* the existence of several modifications is called *isomerism*. What substance have we studied which exists in isomeric modifications?

Rub the head of a match gently with the moistened finger. Notice the odor. (?) Consult the instructor about the preparation of ozone by the action of phosphorus on the oxygen of the air.

EXPERIMENT 28.—**Hydrogen peroxide.**—Examine commercial hydrogen peroxide. Pour a little of it upon some manganese dioxide in a test-tube and test the gas given off with a spark. (?) Take about 25 c.c. of hydrogen peroxide in a beaker and dissolve in it a piece of sodium hydroxide about 1 cm. in length. This is to neutralize the acid which hydrogen peroxide always contains, and which would interfere with the experiments. Add some of this liquid to some water weakly colored with aniline red. (?) Be sure that the water does not contain any solid aniline red at the bottom, for if it does, the solid will continually dissolve and spoil the result.

Put the rest of your hydrogen peroxide into a wide test-tube provided with a cork and a delivery tube leading to a vessel full of water. Boil gently and collect the gas in inverted test-tubes filled with water. Test the gas with the spark. (?) *Only the hydrogen peroxide takes part in the change.* What has happened? What remains in the

test-tube in which the hydrogen peroxide was boiled? Why is the cork frequently driven out of the stock-bottle of hydrogen peroxide?

State *precisely* the relation in composition between hydrogen peroxide and water. State *precisely* what is meant by catalytic action, using hydrogen peroxide as an illustration.

PROBLEMS

10. If 75 c.c. of oxygen could be transformed completely into ozone, what volume of ozone would be obtained ?

11. 115 c.c. of oxygen were partly converted into ozone. The volume contracted to 110 c.c., but when the gas was gently heated by a burner flame the original volume was exactly restored. Calculate (*a*) the volume of ozone which had been produced and (*b*) its percentage by volume in the gas.

12. 160 c.c. of oxygen containing ozone were heated. The volume became 170 c.c. (*a*) How many c.c. of ozone and (*b*) what percentage of it by volume were present ?

CHAPTER VII

COMBUSTION

EXPERIMENT 29.—**Combustion.**—Fit up a lamp chimney with a perforated rubber cork and tube for supplying gas (Fig. 19, p. 52, Part I). Cover the chimney with a piece of asbestos having a hole in it large enough to admit your spoon. Clamp the chimney at its upper portion and see that the cork is tightly placed in the bottom. Use illuminating gas—not hydrogen—and make the experiments on combustion described in Chapter VII, paragraphs 62 and 63, Part I.

In the experiment with nitric acid use *fuming nitric acid.* The ordinary acid is not strong enough for the pur-

pose. Keep the burning substances out of contact with the glass to avoid breakage. Always hold your spoon by the upper end, and keep the hand some distance above the chimney, to avoid burning the fingers.

In getting the oxygen flame (Fig. 20, Part I) use a mouth blowpipe the tip of which has been carefully bent until it is parallel with the longer portion. Connect this with an oxygen cylinder and obtain the gentlest current of oxygen possible. Test the strength of the current by letting it blow on the moistened finger. Insert the blowpipe through the flame into the chimney. *Keep the oxygen flame away from the glass.*

The same chimney can be used for the air-flame; but you will need a doubly perforated cork, one end of which carries a wide, straight tube open at both ends (Fig. 21, p. 55, Part I).

Hold a small crystal of each of the four chlorates mentioned in paragraph 63, Part I, in the lower part of the Bunsen flame with forceps. Record the flame colors of the corresponding metals.

What is a flame? Why do some substances burn with flame and others not? Explain what is meant by the statement that the combustion of one gas in another is reversible. Explain exactly what is meant by the statement that the air flame is the gas flame *turned inside out.*

EXPERIMENT 30.—**The slow combustion of iron.**—Stuff a wad of steel wool about half-way up a tube closed at one end and graduated. Wet the steel and clamp the tube, open end down, in a vessel of water. The level of the water inside the tube must be within the graduations. If it is not, remove the tube from the vessel, pour some more water in the tube, cover the end with the thumb, put it again in the vessel of water and clamp it. Read the level of the water inside the tube, allow to stand for half an hour or as long a time as possible, and read the level

again. Examine the steel carefully. What does the result show? Predict the composition of rust. Was heat evolved or absorbed in this experiment? Steel is chiefly composed of iron, and it was the iron alone which was affected in the experiment. Dislodge the steel wool with the handle of a spoon, or with a glass rod, and clean the tube with a small quantity of strong hydrochloric acid.

CHAPTER VIII

No experiments.

PROBLEMS

Calculate the percentage composition of the substances whose formulas are given below. The amount of each constituent must be obtained by an independent calculation, never by subtracting the sum of the others from 100. State the results to two decimal places. If the third decimal place is greater than 5 add 1 to the second; if less than 5 discard it.

13. Mercuric oxide.......................... HgO
14. Water................................. H_2O
15. Mercuric chloride..................... $HgCl_2$
16. Mercurous chloride .... $HgCl$
17. Potassium chlorate.................... $KClO_3$
18. Table salt (sodium chloride)........... $NaCl$
19. Manganese dioxide.................... MnO_2

Calculate the simplest formulas of the following substances from their percentage compositions.

20. Hydrogen .. 2.74 per cent.	23. Mercury.... 44.07 per cent.
Chlorine ... 97.26 "	Iodine,.... . 55.93 "
21. Nitrogen... 30.43 "	24. Calcium.... 40 "
Oxygen..... 69.57 "	Carbon..... 12 "
22. Carbon..... 40.00 "	Oxygen .... 48 "
Hydrogen.. 6.67 "	25. Potassium .. 52.35 "
Oxygen.... 53.33 "	Chlorine.... 47.65 "

CHAPTER IX

SALT AND SODIUM

Remember the precautions necessary in using sodium (p. 28). Carry out this experiment under the hood. Avoid inhaling chlorine.

EXPERIMENT 31.—**Salt and sodium.**—Fit up the apparatus shown in Fig. 20, and carry out the *synthesis of salt.* The flask should be small. It is one-fourth filled with manganese dioxide in small lumps—not powder. This must be allowed to slide slowly into the flask, the latter being in an inclined position. *The perforated cork and exit tube must fit tightly;* otherwise chlorine will escape and cause great distress and possibly injury. The bulb must be of hard glass. It contains a fragment of sodium the size of a pea, which may be elongated by rolling, to get it into the tube.
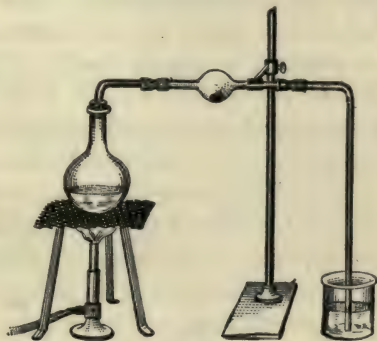
Cover the manganese dioxide with strong hydrochloric acid, place

FIG. 20.

the flask on wire gauze, connect the apparatus, and apply a gentle heat. The tube which is bent downward dips into about 20 c.c. of alcohol or sodium hydroxide solution, which will absorb the excess of chlorine.

When the gas in the bulb appears green (?) heat the sodium very gently with a small flame. When the action begins, stop heating the sodium. When the action is over, extinguish the burner, take out the cork of the chlorine generator and fill the latter with water to stop the evolu-

tion of gas. It is well to do this quickly, to hold the breath during the operation, and to retire ten feet or more for a short time until the chlorine which the water forces out of the flask is dissipated.

Break open the bulb. The black product is *silicon* due to the unavoidable action of the sodium upon the glass. Taste the white product. Is it soluble in water? Is it possible for an insoluble substance to have any taste? Why? What information does this experiment give regarding the composition of salt? Is the information qualitative or quantitative? Throw the fragments of the bulb-tube into a vessel of water to get rid of any sodium which may have escaped the action of the chlorine.

Does salt contain more or less energy than its constituents taken separately? How do you know? If you had to decompose salt into sodium and chlorine, would it be necessary to supply energy or would the decomposition furnish energy which could be applied to other purposes? Recall all the cases in your past work in which you have brought about or witnessed the *combination* of two elements. Was energy absorbed or given out in these experiments? Recall the cases in which a compound has been decomposed. Was energy given out or absorbed? Irritation from chlorine can be relieved by at once inhaling the vapor of alcohol.

EXPERIMENT 32.—**Preparation of pure salt.**—Prepare a saturated solution of salt, filter the liquid, and pass hydrochloric acid-gas into it through an inverted funnel, whose rim just dips into the liquid. The gas is obtained as described on p. 56, Experiment 41, the sulphuric acid being allowed to drop *very slowly* into the hydrochloric. Salt, being insoluble in hydrochloric acid, is precipitated; the other substances present remain dissolved. When enough salt has collected, pour away the liquid and wash the salt three times with very small quantities of dis-

tilled water. (Why is this necessary?) Place the salt in a clean dish and apply heat with a small flame which does not touch the dish, stirring the salt constantly with a glass rod. Preserve the pure salt in a dry, clean test-tube, tightly corked and labelled.

EXPERIMENT 33.—**Sodium.**—Examine sodium, and write a description of it. Cut it. Is it a metal? Why does the luster fade? How could the fading be prevented? Could sodium be used in the same way as iron or copper? Why? How does its density compare with that of familiar metals?

Hold a small fragment of sodium in the flame in forceps. (?) Explain, from previous work, the behavior of sodium with oxygen, with chlorine, and with water. Explain *precisely* what is meant, both qualitatively and quantitatively by the equation—

$$Na + H_2O = NaOH + H$$
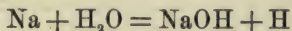
EXPERIMENT 34.—**Sodium compounds.**—*Sodium hydroxide must not be touched with the fingers. The bottle containing it must be kept tightly corked.* Examine sodium hydroxide, sodium nitrate, sodium carbonate (anhydrous), sodium carbonate (crystallized), and sodium sulphate. Are they soluble in water? What color does each communicate to the flame? Use a clean iron wire hot enough to make a fragment of the sodium compound adhere to it. After the test, clean the wire by dipping it into a little hydrochloric acid in a test-tube (*not in the bottle*) and holding it in the flame until the latter shows no color, and use it to test the next substance.

Prepare a solution of sodium hydroxide by dissolving a piece about 1 cm. long in 50 c.c. of water in a beaker. Test small separate portions of it with blue litmus paper, with red litmus paper (use small pieces), with a drop of phenol phthalein solution, with a drop of cochineal solu-

tion. What are the results? Liquids which affect these coloring matters in this way are called *alkaline*.

Place the rest of the sodium hydroxide solution in a clean dish and add hydrochloric acid to it one drop at a time. After each drop stir with a glass rod and test the liquid with a fragment of blue litmus paper. When the paper is just turned red, remove it and evaporate the liquid carefully to dryness. Turn down the flame very much toward the end and keep it moving. Taste the residue when it is perfectly dry. What is it? What other product must have been formed? Write the equation.

Expose a clean crystal of sodium carbonate and a piece of sodium hydroxide on two separate watch glasses to the air for an hour or overnight. What happens? What is meant by efflorescence? by deliquescence? What has the state of the air to do with both? How would any soluble salt behave if kept in an atmosphere saturated with water-vapor?

EXPERIMENT 35.—**Sodium carbonate. Sodium acid carbonate.**—Stir up some ammonia water with salt in a beaker until the solution is saturated. Let the undissolved salt settle and pour off the solution into another beaker. Pass carbon dioxide into it through a funnel the rim of which dips into the liquid. The carbon dioxide can be obtained from a Kipp generator or made in a gas-generating bottle from marble and dilute hydrochloric acid as directed on p. 133, Experiment 127. The precipitate is sodium acid carbonate (baking soda), $NaHCO_3$. Filter and dry the product by pressing it between layers of filter paper, which are renewed as they become wet.

Arrange a test-tube with a cork and a delivery-tube dipping into a little lime-water. Place some dry sodium acid carbonate in it, support the tube horizontally, and apply a very gentle heat. What gas is given off? What condenses in the tube? Compare the residue in the tube

with anhydrous sodium carbonate, Na_2CO_3. Write the equation.

These two reactions illustrate the *ammonia soda process,* the most important method of manufacturing sodium carbonate.

Make a mixture of sodium acid carbonate with about twice its weight of cream of tartar. Grind the two together in a dry mortar. What familiar substance have you made? Is there any action? As a rule, chemical action between solids at ordinary temperature and pressure is slow, so slow that it is almost imperceptible. Place some of the mixture in a test-tube and add water. (?) Fit a cork bearing a delivery tube to the test-tube and pass some of the gas into lime-water. (?) What is the function of this gas in the baking process? The same gas is produced when sodium acid carbonate is treated with an acid—e. g., hydrochloric acid. (Try it.)

EXPERIMENT 36.—**Water of crystallization.**—Examine some crystallized copper sulphate. Place about 2 grams of it in a dry, clean dish, cover with a dry, clean beaker, and heat by a small flame, kept in motion. (?) After about five minutes, remove the beaker and heat the substance a little more intensely, stirring it and pressing the lumps gently with a glass rod. Let the product cool and compare it with the original substance. What is it? Sprinkle some water upon it. (?) It becomes hot. What is the source of the heat? What is water of crystallization and why is it so called? From the facts furnished by this experiment, discuss the question whether water of crystallization is chemically combined or merely mixed.

PROBLEMS

26. Calculate the percentage composition of
    a. Sodium carbonate............... Na_2CO_3,
    b. Cystallized sodium carbonate..... $Na_2CO_3, 10H_2O$.
In *b* calculate *water,* not hydrogen.
    26

27. How much sodium carbonate can be made from 10 kilos of salt?

28. How much sodium is necessary to decompose 36 grams of water, and how much hydrogen is liberated?

29. How much sodium can be obtained by the electrolysis of 20 grams of sodium hydroxide?

30. A piece of sodium was placed in water. 500 c.c. of hydrogen under standard conditions escaped. What was the weight of the sodium?

31. How much sodium carbonate and slaked lime are needed to make 2 kilos of sodium hydroxide?

CHAPTER X

CHLORINE

EXPERIMENT 37.—Chlorine.—*Carry out this experiment under the hood. Avoid inhaling the gas. Be sure that the cork of the apparatus fits tightly. If the throat becomes irritated, place some alcohol in a beaker or on a handkerchief and inhale the vapor.*

Place crystals of potassium permanganate 1 cm. deep in a flask ($\frac{1}{2}$ liter capacity or less). The substance need not be pure. Fit the flask with a rubber stopper carrying a dropping funnel and a delivery tube. Support it firmly on wire gauze, and put a small flame 8 cm. below it. Allow hydrochloric acid to fall drop by drop into the flask. Collect by downward displacement four wide test-tubes and four bottles full of the gas. Judge when the vessel is full by the color, and *immediately* cover it tightly with a glass plate and substitute another; otherwise the excess of chlorine will be forced out at the top and make the air unfit to breathe. Test-tubes full of chlorine can be corked. The exit tube of the chlorine apparatus must reach to the bottom of the vessel. This tube should be cut about a foot

from the desk and united again by a short piece of rubber tube, that it may be moved without disturbing the apparatus. The vessel in which you are collecting chlorine should be kept covered, and the exit tube slipped between the cover and the side of the bottle. The bottles of chlorine must be kept covered during all experiments. When you have finished and desire to get rid of the chlorine, place the bottles under the hood, remove the covers without breathing, and at once retire to a distance. After the chlorine has escaped—which will require ten minutes—the bottles can be cleaned.

Record the physical properties of the element. Invert a test-tube full in water and shake gently. Is it soluble? Into a test-tube filled with the gas throw a pinch of powdered arsenic. (?) Into another test-tube a little powdered antimony. (?) Fill a *small,* clean test-tube with hydrogen from the Kipp apparatus by upward displacement. Without losing any of either gas, bring this tube mouth to mouth with a test-tube filled with chlorine. The two tubes should be of the same size, and the tube containing the hydrogen uppermost. Keeping the mouths together, invert several times to mix the gases, then hold the mouth of each tube to a flame. This experiment must not be made in direct sunlight. Why not? What is the product?

Lower a hydrogen flame into a bottle of chlorine. If you use a gas-generating bottle in this experiment, remember that it must be allowed to run five minutes and that the generator and stopper must be wrapped in a towel before lighting the hydrogen. Describe the appearance of the flame of hydrogen burning in chlorine. Hold a glass rod bearing a drop of ammonia near an open bottle of hydrochloric acid. (?) This is a *test* for hydrochloric acid. Now hold a drop of ammonia in the gas left in the jar in which the hydrogen was burned. Is it hydrochloric

acid? Has it the color of chlorine? Heat a piece of charcoal in a spoon until it begins to burn, and place it in chlorine. (?)

Take out the charcoal and lower a lighted candle supported on a wire into the same bottle of chlorine. The candle is composed chiefly of compounds of hydrogen and carbon. The black substance thrown off from the flame is carbon (soot). Use the two preceding results to explain this one. What else must be produced? Let the covered jar stand till the soot settles and try the test with the glass rod bearing a drop of ammonia.

In the third bottle place a bit of red litmus paper, a piece of blue litmus paper, a strip of colored calico, and a fragment of printed matter smeared over with writing ink until it is illegible. Describe and explain the results. What is the most important use of chlorine?

In the fourth bottle place some fresh slaked lime (milk of lime answers well) and immediately cover the bottle tightly with the palm of the hand and shake it. (?) Does the chlorine disappear?

Carefully add nitric acid, a few drops at a time, to the contents of the bottle. What happens? What very important technical process does this illustrate?

EXPERIMENT 38.—**Chlorine water. Bleaching.**—Prepare some chlorine water by passing chlorine made as in Experiment 37 into cold water under the hood for twenty minutes. You will need about 500 c.c. Examine it. Has it any of the properties of the gas? Does it bleach? Try small portions of it with red and blue litmus paper. With a drop of ink.

Select a tube of soft glass 1 cm. or more wide and about 1 meter long. Seal it near one end by drawing it out in the flame of the blast lamp. Cover it with soot with the yellow flame before cooling, to avoid cracking. When cool wash off the soot, fill the tube with chlorine

water and invert it in the same liquid in a glass or porcelain dish. Clamp vertically and allow to stand in direct sunlight as long as possible.

When a sufficient quantity of gas has collected, cover the end of the tube with the thumb, remove it from the dish and test the gas with the spark. Explain what has happened.

Prepare a thin paste of bleaching powder and water in a small beaker or dish. Add a few drops of sulphuric acid (why?) and soak in the liquid a small piece of some colored cotton fabric (calico) or a piece of litmus paper.

EXPERIMENT 39.—**Combustion of chlorine in hydrogen.** (*Use the hood in this experiment.*)—Generate chlorine from coarsely powdered manganese dioxide and strong hydrochloric acid in a wide test-tube, which must not be more than one-third filled with the mixture. The tube is clamped upright and is closed by a perforated cork bearing a straight narrow tube about 20 cm. long ending in a jet. Have ready a bottle of hydrogen, standing in water. Apply a gentle heat to the chlorine generator, and when the gas over the liquid is green and chlorine is escaping freely, light the hydrogen, holding the bottle inverted, and instantly slip the bottle over the jet of chlorine. Taken in connection with the burning of hydrogen in chlorine, what does the result show? Test the product in the bottle with a drop of ammonia on the end of a glass rod.

Fill the test-tube with cold water to stop the production of chlorine.

Sum up all the evidence you have obtained thus far bearing upon the composition of hydrochloric acid.

EXPERIMENT 40.—**Electrolysis of hydrochloric acid.**— Place about 200 c.c. of strong hydrochloric acid in a beaker and dilute it with about ¼ of its volume of water. Add a handful of salt and stir for five minutes to saturate the liquid. Pour off the clear liquid and introduce it into

the apparatus shown in Fig. 2, Part I, which you have already used for the electrolysis of water. The salt takes no part in the change. Its object is to reduce the solubility of the chlorine in the water present.

Allow the current to pass. Allow some of the gases to collect. Notice the color, and, cautiously, the odor of both. Remember that a colored gas may appear colorless in a thin layer. Look *along* the tube as well as through it. Try to burn each gas, using a very short rubber tube with a short jet, as in the electrolysis of water. Try the action of both gases upon paper wet with a solution containing potassium iodide and starch. After the apparatus has been running about half an hour, let the gases collect for a time and measure the quantity of each. Is the result exactly what you expect? If not, explain.

EXPERIMENT 41.—**Preparation and properties of hydrochloric acid.**—Prepare hydrochloric acid from commercial hydrochloric acid solution and strong sulphuric acid as directed on p. 81, Part I. A flask closed by a doubly perforated cork carrying a separating funnel and a delivery tube is sufficient. The sulphuric acid must be allowed to drop slowly into the hydrochloric, and the delivery tube must be *dry*. Collect by downward dry displacement in bottles, which must be perfectly dry. (Why?) Keep the bottles covered during the collecting and afterward.

What are the color and odor of the gas? Is it soluble in water? Bring the mouth of a bottle of the gas near the surface of water, remove the glass plate and then plunge the bottle into the water. Do not remove the plate under the water. The sudden inrush of water is likely to break the plate and cut the hand. Wrap the bulb of a thermometer in damp filter paper and introduce it into a bottle of hydrochloric acid. Is there any alteration in temperature? Explain. Does the gas burn?

Does it support combustion? Lower a lighted candle on a wire into a bottle of it. In another bottle place a strip of red and a strip of blue litmus paper. (?) Into another bottle throw a wad of filter paper wet with ammonia. (?)

EXPERIMENT 42.—**Preparation of sodium amalgam.**— Weigh out roughly on the trip-scales in a dry beaker about 200 grams of mercury. Weigh also 1.5-2 grams of sodium and cut it into pieces about half the size of a pea. Place the mercury in a clean dry mortar, add one piece of sodium and press it under the mercury with the pestle until there is a flash and a little smoke, showing that the reaction has occurred. Mercury vapor is poisonous, and it is well therefore to do this under the hood. Continue in this way until all the sodium is introduced. The amalgam should still be liquid. If it is solid, too much sodium has been used and it is necessary to add more mercury and mix thoroughly with the pestle. Sodium amalgam, like sodium, is acted upon by moist air and must be preserved in a tightly closed bottle. Its chemical action is simply that of the sodium it contains, but the presence of the mercury makes the reactions less violent.

EXPERIMENT 43.—**Analysis of hydrochloric acid.**— Allow 10 c.c. of water from a pipette or burette to run into a small clean test-tube and mark the level of the water by a narrow strip of gummed label. Dry the tube thoroughly with paper or cloth, not with the flame. Select a straight graduated tube of about 50 c.c. capacity sealed at one end. The portion nearest the open end will not be graduated. Ascertain its capacity by taking the length from the end of the graduation to the end of the tube in compasses or with a strip of paper and transferring it to the scale on the tube. Add this to the graduated portion to ascertain the total capacity of the tube.

The tube must be perfectly dry. Fill it by downward displacement with hydrochloric-acid gas, generated as in

Experiment 41, and dried by passing through a U-shaped tube containing bits of broken glass tubing wet with strong sulphuric acid. Since the presence of air will spoil the result, the generator must be run until all air is expelled from it and the graduated tube—five minutes or more. The use of the hood will save discomfort. The exit tube must run to the bottom of the graduated tube and must be withdrawn gradually while the generator is still running, otherwise it would leave a vacancy which would be filled with air. Have at hand 10 c.c. of sodium amalgam in the measuring test-tube and *at once* introduce it and cover the tube tightly with the thumb. Let the sodium amalgam fall the length of the tube a dozen times or more to make the action complete, bring the open end of the tube under water in a cylinder, remove the thumb, lower the tube until the level of the water is the same inside and out, and clamp it. Allow to stand five minutes and read the volume of the gas.

Cover the tube with the thumb, remove it from the water, invert it and apply a flame to the residual gas. (?) Calculate thus:

Volume of tube to end of graduated portion ..... 50 c.c.
Capacity of ungraduated portion................. 12 "

    Total capacity............................ 62 "

Since the 10 c.c. of sodium amalgam introduced
    expel 10 c.c. of gas, the volume of hydrochloric
    acid taken was 52   c.c.
The tube at the end of the experiment contained 26.4 "

Hence the proportion of hydrogen by volume contained in hydrochloric acid is $\frac{26.4}{52}$, or about $\frac{1}{2}$.

EXPERIMENT 44.—**Action of sulphuric acid on salt.**— Place a handful of salt in a wide-mouth bottle and allow a little strong sulphuric acid to drop upon it. Cover the

bottle. Is heat produced? Sink a lighted candle in the bottle. (?) Blow across the mouth of it. Hydrochloric acid causes fumes in moist air, because it causes the water-vapor to condense, forming a solution of hydrochloric acid. Hold a drop of ammonia in the bottle. (?)

What substance would remain in the bottle if the action of the sulphuric acid was complete? Write the equation. Place about 25 c.c. of water in a beaker. Stand the beaker in a pan of cold water and slowly pour in 50 c.c. strong sulphuric acid stirring constantly. Let the liquid cool *completely* and pour it slowly upon about 30 grams of salt in a small flask provided with a well-fitting cork and delivery tube. This tube must be perfectly *dry,* for any water will absorb the gas. Apply a gentle heat. Be careful not to let the liquid boil over. Collect the hydro-chloric-acid gas in dry test-tubes and bottles. The delivery tube must reach to the bottom of the bottle. Is it soluble in water? Try it by placing a test-tube filled with it mouth downward in water. How does it affect red and blue litmus paper? Does it burn? Does it support the combustion of a candle? Pour some ammonia-water on a wad of filter paper and throw it into a bottle of the gas. (?) What is left in the generating flask?

Pour the material in the flask down the sink, running abundant water at the same time, and again put in salt and dilute sulphuric acid in exactly the same way. Pass the gas into a small inverted funnel whose rim dips into water in a dish and whose stem is connected by a rubber tube with the delivery tube. Continue until the materials are exhausted. Use the hydrochloric acid prepared in this way for Experiment 45.

EXPERIMENT 45.—**Action of hydrochloric acid upon metals.**—Try the action of hydrochloric acid upon small quantities of zinc, magnesium, aluminium, and copper. Place the metal in a test-tube, cover it with water, and

gradually add hydrochloric acid solution. If gas is produced test it with a flame. (?) What is the other product of each case? Try the action of hydrochloric acid upon a fragment of marble.

QUESTIONS

Answer these questions as briefly as possible. If you know the equation for the change you desire to explain that alone will suffice, but *never invent equations or formulas*. Remember that a formula is a faithful description of the composition of a real compound. Mere arbitrary collections of symbols are worse than meaningless—they are absurd. Never write an equation in your notes unless you are sure, first, that every formula it contains is that of a real substance ; second, that the number of symbols of each kind is the same on both sides of the sign of equality ; third, that the equation describes a process which you know from laboratory or lecture-table experiments to be a real chemical change. Unless the equation satisfies these requirements, discard it, and describe the change briefly in words. Some of the questions can be answered in a number of different ways, all of which are correct.

1. How could you convert the hydrogen of hydrochloric acid into water ?

Answer

$$Zn + 2HCl = ZnCl_2 + H_2.$$
$$H_2 + O = H_2O.$$
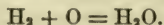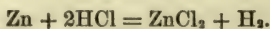
In words, the answer would be : Zinc will liberate the hydrogen, forming zinc chloride. The hydrogen can then be burned in the air to water.

2. How would you make Na_2SO_4 from $NaCl$?

3. How could you prepare water, taking the hydrogen from sulphuric acid and the oxygen from copper oxide ?

4. Prepare water, taking the hydrogen from sulphuric acid and the oxygen from potassium chlorate.

5. Prepare arsenic chloride, taking the arsenic in the free state and the chlorine from sodium chloride.

6. How could you convert the oxygen of potassium chlorate into ozone ?

7. Obtain hydrochloric acid, taking the hydrogen from water.

8. Convert the oxygen of water into copper oxide.

Problems

32. What weight of chlorine can be obtained by heating 12.5 grams of manganese dioxide with an excess of hydrochloric acid ?

33. How much manganese dioxide is needed to make 25 grams of chlorine from hydrochloric acid ?

34. How much aqueous hydrochloric acid containing 20 per cent HCl is required to liberate 100 grams of chlorine with manganese dioxide ?

35. 20 c.c. of chlorine were mixed with 16 c.c. of hydrogen and the mixture exploded. What volumes of what gases remained in the vessel ?

36. Hydrogen was burned in chlorine and the hydrochloric acid produced collected. It weighed 146 grams. What weights of both gases had been consumed ?

37. 50 grams of sodium hydroxide are dissolved in water and the solution mixed with a solution containing 50 grams of pure hydrochloric acid. What substances, and how much, will be contained in the resulting liquid ? Do not calculate water.

38. 32.75 grams of zinc are dissolved in hydrochloric acid. What weights of zinc chloride and hydrogen are produced ?

39. 40 grams of magnesium are allowed to dissolve in hydrochloric acid. Calculate the weights of hydrogen and magnesium chloride produced.

CHAPTER XI

CHLORIDES—COMPOUNDS OF CHLORINE CONTAINING OXYGEN

EXPERIMENT 46.—**Preparation of chlorides.**—Place about 1 gram of zinc oxide in a test-tube, cover with water, and add hydrochloric acid. If necessary, heat gently, but not to boiling. What is produced? Is gas evolved? What becomes of the hydrogen of the acid? Repeat, using magnesium oxide. Write the equations.

Make a strong solution of sodium hydroxide and slow-

ly add an excess of hydrochloric acid, stirring constantly. Write the equation.

Examine a fragment of marble. Coarsely powder a little. Is it soluble in water? Add some hydrochloric acid to the water. (?) When the action is over, evaporate the liquid to dryness in a dish. Is the residue soluble in water? Is it marble? Write the equation.

State four methods by which the salt of a given metal and a given acid can be prepared, and give an example of each.

EXPERIMENT 47.—**Insoluble and slightly soluble chlorides.**—To a dilute solution of silver nitrate, $AgNO_3$, add a little hydrochloric acid. The precipitate is silver chloride, $AgCl$. Write the equation. Divide the liquid containing the precipitate into three parts. Expose one portion to sunlight, or the brightest light attainable. With the second ascertain whether silver chloride is soluble in nitric acid. With the third investigate its solubility in ammonia.

Mix a few drops of silver nitrate solution with some solution of sodium chloride. What is the precipitate? Prove it. Any soluble chloride would produce the same effect upon silver nitrate.

Precipitate a little solution of *mercurous nitrate,* $Hg_2(NO_3)_2$, with hydrochloric acid. The precipitate is mercurous chloride, Hg_2Cl_2. Divide the liquid containing the precipitate into two parts. With one ascertain the action of strong light. Expose for some time. Treat the other with ammonia. What are the results? How can mercurous chloride be distinguished from silver chloride?

Make a solution of lead nitrate, $Pb(NO_3)_2$, and add hydrochloric acid to it. The precipitate is lead chloride, $PbCl_2$. Write the equation. Heat the liquid containing the lead chloride to boiling and stand it aside to cool. Is lead chloride soluble in cold water? In hot water? How

could lead chloride be separated from silver chloride? From mercurous chloride? Devise a method of separating a mixture of the three chlorides.

EXPERIMENT 48.—**Chlorine peroxide.**—Make the experiments described in paragraph 112, Part I. Use a cylinder of not more than 200 c.c. capacity and *not more* than 0.5 gram of finely powdered potassium chlorate. Cover the bottom of the cylinder with sulphuric acid and introduce the chlorate gradually.

EXPERIMENT 49.—**Potassium chlorate.** *Potassium hydroxide must not be touched with the hands. Use paper or forceps in handling it. Make this experiment under the hood.*—Dissolve about 40 grams of potassium hydroxide in about 100 c.c. of water in a dish and pass chlorine into the liquid through an inverted funnel whose rim dips under the liquid. From time to time test the liquid with a strip of red litmus paper, and when the latter is no longer turned blue (?) stop the chlorine. Pour off the liquid from the white crystals in the dish and dissolve the latter in the smallest possible quantity of hot water. If anything remains undissolved, remove it by filtering the hot liquid, then let the liquid cool. Collect the product which separates on a filter, and dry it between layers of filter paper. Examine it and compare its appearance with that of potassium chlorate. What is the effect of heat upon it? Use a tube sealed at one end and test the gas given off by the spark. Unless your substance was perfectly dry, water will appear in the sealed tube, but it is not a product of the chemical change and can be disregarded.

What is the action of sulphuric acid on the substance you have made? *Use very small quantities.*

How is potassium chlorate made at present, and what are its chief uses?

QUESTIONS

1. Why is no gas given off when an oxide or a hydroxide is treated with hydrochloric acid ?

2. What is the real meaning of the expression "insoluble" ?

3. How could sodium chloride be converted into sodium nitrate ?

4. Does chlorine peroxide, ClO_2, contain more or less energy than chlorine and oxygen separately ?   How do you know ?

5. Construct, in the form of a table, a brief comparison of the four elements already studied.

PROBLEMS

40. Calculate the percentage composition of bleaching powder, $CaOCl_2$.

41. Determine the name and formula of a compound having the following composition :

Sodium	21.60 per cent.	
Chlorine	33.33	"
Oxygen	45.07	"

42. 25 grams of pure marble are dissolved in hydrochloric acid. What are the products and how much of each is produced.   How much HCl is consumed ?

CHAPTER XII

No experiments.

QUESTIONS

1. What are the two possibilities regarding the nature of matter ?

2. What is a molecule ?   Is a molecule a thing or an idea ? Why ?

3. What is the evidence which causes us to consider the molecule to be composed of smaller particles ?

4. Explain precisely what is meant by the term *atomic weight*.

5. State the chemical laws in the language of the atomic theory.

6. Suppose that some one should succeed in transforming lead

into gold - a highly improbable supposition : what changes in the atomic theory would have to be made to explain the discovery ?

CHAPTER XIII

EXPERIMENT 49*a*.—**Analysis of the air by means of phosphorus.**—*Phosphorus catches fire spontaneously, and to leave it lying around or put away any of it under the desk would be likely to cause the destruction of the building. Burns made with it are poisoned wounds which heal with great difficulty. It must be kept, cut, and handled under water, and the hands must be freed from it before they are brought into the air. Be careful not to get it behind the nails. If it should catch fire while you are working with it pour water upon it.*

The method is to absorb the oxygen from a measured volume of air, confined over water, by means of phosphorus. The residual gas, consisting chiefly of nitrogen, is again measured. The experiment is shown in Fig. 27, Part I. The water used must have stood in the laboratory a day or two so as to acquire the temperature of the room. The jar should be wide, so as to allow freedom to the hand.

Fill the graduated tube with water, close the end with the thumb and put it, open end down, into the jar of water. Catch hold of the upper part of the tube with a paper holder—*not with the hand*—and allow 20 c.c. to 30 c.c. of air to enter the tube. Hold the tube so that the level of the water inside and outside is the same, and measure the volume of air. Repeat the measurement to be sure there is no error.

Now bend a wire to the shape shown in the cut and

fasten a small piece of phosphorus to it, working under water in a tin pan or other large vessel. Transfer the wire to the jar and push the phosphorus up into the air in the graduated tube, taking care to keep the open end of the tube constantly under water. Let the apparatus stand for an hour and examine it. If the water has reached the phosphorus raise the latter so as to keep it in the air. Next morning pull the phosphorus down into the water and make the level of the water inside and outside the same. This must be done without touching the tube with the fingers. Read the volume of the residual gas. The loss in volume is *oxygen*. Calculate the percentage of oxygen by volume in the air thus:

$$\frac{\text{Volume of oxygen} \times 100}{\text{Volume of air}} = \text{per cent of oxygen.}$$

Plunge a burning splinter into the gas remaining in the tube.

In this method errors result from changes in atmospheric pressure and temperature between the two measurements. If a more accurate result is desired, a thermometer must be placed in the jar ten minutes before the volume of the air is measured in the first place. Temperature and barometer pressure must be read and recorded and the volume of the air reduced to standard conditions by the method explained in the Appendix. Temperature and pressure must again be read at the time the residual gas is measured and its volume also reduced. Then this reduced volume is subtracted from the other and the calculation made as before.

EXPERIMENT 49*b*.—**Analysis of the air. Alternative method.**[1]—Use a graduated tube holding 50 c.c., like that

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[1] This method is at least as accurate as that described in 49*a*, and much more rapid. It has the advantage of not requiring the use of phosphorus.

employed in Experiment 43. Ascertain the capacity of the ungraduated portion. Have ready a cork which fits the tube *tightly*. If a wooden cork, it must be well rolled under the foot. A rubber cork without any perforation is best. Make a measuring test-tube to hold 10 c.c., as described in Experiment 43. It need not be dry.

Dissolve a small piece of potassium hydroxide in about 15 c.c. of water in a beaker and add to the liquid about 0.5 gram of *pyrogallic acid. Use the solution at once. It spoils rapidly.* Take 10 c.c. of this liquid in your measuring test-tube, pour it into the graduated tube, and instantly cork the tube tightly. Make the liquid flow from one end of the tube to the other twenty times or more. Place it in a deep cylinder of water, cork down, remove the cork, allow to stand five minutes, equalize the levels without touching the part of the tube containing the nitrogen with the hand and read the volume. Calculate thus:

Capacity of tube to end of graduations..... 50 c.c.
Capacity of ungraduated portion.......... 9 "

Total capacity....................... 59 "

Since 10 c.c. of liquid was introduced, the volume of air taken was 59 − 10, or 49 c.c.

Volume of gas left in the tube, 38.5 c.c.

The loss in volume is oxygen. This is

$$49 - 38.5 = 10.5 \text{ c.c.,}$$

and the percentage of oxygen is

$$\frac{10.5 \times 100}{48.5} = 21.4 \text{ per cent.}$$

EXPERIMENT 50.—**Eudiometric analysis of air.**—In this experiment the U-shaped eudiometer described in Experiment 9 is used. If no Kipp generator is available, have ready a wide test-tube with a delivery tube ending in a short piece of rubber tubing. This test-tube should con-

tain a little zinc covered with water and is to be used as a source of hydrogen.

Clamp the eudiometer (Fig. 9) vertically and fill both limbs of it with mercury. Open the stop-cock S, place a dry, clean beaker under C and allow mercury to run out until about 20 c.c. of air has entered the tube. Close C and measure and record the volume of the air. Verify the measurement. Turn S so that the air in the eudiometer is isolated and so that gas passed in at T will escape at E. Pass hydrogen through the stop-cock for three minutes, allowing it to escape into the air. Then pass not more than 15 c.c. nor less than 10 c.c. of hydrogen into the eudiometer, turn the stop-cock so as to close the eudiometer, and *at once* remove the generator. Equalize the mercury levels in both limbs by running out mercury carefully from C. If too much mercury is run out, pour some in at the top of the open limb and again equalize. Read off the volume and record it as air + hydrogen.

Press the thumb tightly on the open end of the eudiometer and pass the spark from an induction-coil excited by three Edison-Lalande cells, two bichromate cells, or in any other suitable way. What is the cause of the explosion? Pour mercury in the open limb until the level is slightly higher than that in the other, and let the apparatus stand for five minutes. (?) Equalize the levels exactly by running out mercury from C, and read and record the " volume after explosion." Calculate as in the following example:

$$
\begin{aligned}
\text{Volume of air taken} &\ldots\ldots\ldots\ldots\ldots\ 25 \text{ c.c.} \\
\text{Volume of air} + \text{hydrogen} &\ldots\ldots\ldots\ 39 \text{ "} \\
\text{Volume after explosion} &\ldots\ldots\ldots\ldots\ 23.4 \text{ "}
\end{aligned}
$$

The loss in volume after explosion must be $\overline{15.6}$ "

Now this contraction is due to the disappearance of oxygen and hydrogen to form water, and in this reaction

one volume of oxygen and two of hydrogen disappear. Hence the volume of the oxygen in the air taken must be $\frac{15.6}{3} = 5.2$ c.c., and the percentage must be $\frac{5.2 \times 100}{25} = 20.8$ per cent.

This method of analyzing the air is employed in actual work, since it is rapid, and, with proper care, accurate.

EXPERIMENT 51.—**Absorption of the oxygen of the air by metals.**—The method is to pass air over a column of copper filings heated nearly to redness in a tube similar to that used in Experiment 10, Fig. 11. The tube should be about 30 cm. (12 inches) long, and about 20 cm. (8 inches) of it should be heated nearly to redness by a wing-top burner with several chimneys. The copper filings are held in place by loose plugs of asbestos, and after being filled the tube should be held horizontal and tapped gently on the table to make a channel along the upper portion.
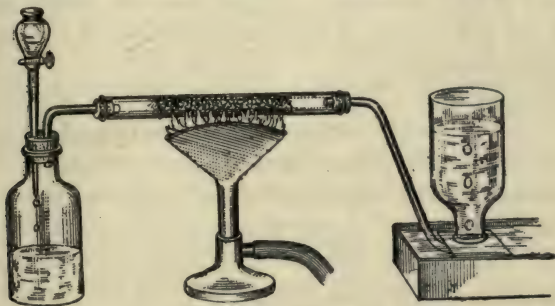
FIG. 21.

One end of the tube is connected with a bottle out of which air is expelled by water, which is allowed to drop into the bottle from a separating funnel which passes through the stopper. The air passes over the hot copper, which absorbs the oxygen, and the nitrogen is collected over water. The apparatus is shown in Fig. 21. The bottle from which the air is expelled and that in which the nitrogen is col-

lected should be of the same size and shape. The speed
of the current of air depends upon the rate at which the
water is allowed to fall upon the separating funnel. *It
should be as slow as time permits.*

What change takes place in the copper? At which end
of the tube does the change begin? About what fraction
of the air disappears?

When the experiment is finished, slip a glass plate over
the bottle of nitrogen and remove it from the water.
Plunge a burning piece of wood or a lighted candle into
the gas. (?) What is the effect of the nitrogen of the
air upon combustion processes, and how is this effect
caused?

Repeat the whole experiment, using iron filings instead
of copper. Explain exactly what takes place.

EXPERIMENT 52.—Expose some clear lime-water in a
beaker to the air for some time. Look for a change at the
surface of the lime-water. What does the result prove?
What are the sources of the carbon dioxide of the air and
what becomes of it?

EXPERIMENT 53.—**Nitrogen.**—Put about 5 grams of
ammonium chloride and the same quantity of powdered
sodium nitrite, $NaNO_2$, in a small flask and add enough
water to make a thin paste. Set up the apparatus as shown
in Fig. 28, Part I. Apply a gentle heat and collect the
nitrogen over water. *Stop heating as soon as the reaction
begins or it will become too violent.* If the evolution of
gas threatens to become too energetic, immerse the gen-
erating flask *for an instant only* in a pan of cold water,
which should be in readiness. This will immediately quiet
it. *Long immersion will cause water to flow back into
the flask and spoil the experiment.*

What are the physical properties of the substance you
have prepared? Does it burn? Does it support the com-
bustion of a candle?

Questions

1. What constituents of the air are essential to life, and why ?

2. What are the reasons for the belief that the air is a mixture, not a compound ?

3. Describe an experiment which proves that the air contains the vapor of water.

4. Nitrogen is lighter than oxygen and water-vapor only about half as dense. On the other hand, carbon dioxide is much denser than oxygen. Why is it that all these substances remain uniformly mixed in the air and do not separate into layers according to density ?

5. What is the effect of the nitrogen of the air upon combustion processes, and why ?

6. Is there any difference between nitrogen obtained from the atmosphere according to Experiment 51 and that prepared by chemical methods as in Experiment 53 ? Why ?

7. What elements are most abundant in the bodies of animals and plants ?

Problems

43. 16.7 c.c. of air were confined over mercury in a eudiometer and enough hydrogen added to make the volume 30 c.c. After explosion, the volume was 19.5 c.c. What percentage of oxygen by volume did the air contain ?

44. 20 c.c. of air are mixed with 10 c.c. of hydrogen and the spark is passed. After the explosion, what volumes of what gases remain in the tube ?

In solving this problem assume that the air contains 21 per cent by volume of oxygen.

45. 2 liters of air were passed over hot copper. The increase in weight of the copper was .6 gram. What was the percentage of oxygen by weight in the air ?

Assume the weight of 1 liter of air to be 1.293 grams.

46. What weight of nitrogen can be obtained by heating 13.8 grams of sodium nitrite, $NaNO_2$, with the required quantity of ammonium chloride, NH_4Cl ? How much ammonium chloride is needed ? What weights of salt and of water are formed ?

CHAPTER XIV

AMMONIA

EXPERIMENT 54.—**Preparation of ammonia gas.**—Place about 150 c.c. of ammonium hydroxide in a 500 c.c. flask. Arrange the apparatus as shown in Fig. 30, Part I. A little mercury should be placed in the bend of the safety-tube. A piece of asbestos board must be placed under the flask. Use glass tubing as far as possible in constructing the apparatus. A rubber cork can be used in the flask.

Apply a gentle heat and collect the ammonia by *upward* displacement in bottles, which must be *absolutely dry.* Why? The tube must run up to the bottom of the inverted bottle. From time to time hold a drop of hydrochloric acid on a glass rod to the mouth of the bottle. Dense white fumes indicate that the latter is full and ammonia is escaping. Collect three bottles of the gas and stand them on glass plates in inverted position. Hold the exit tube of your apparatus to the burner flame. How does the gas behave as regards combustion? Does it produce a continuous flame? Can it be made to do so? What are the products of its combustion?

Plunge the mouth of a bottle filled with the gas under water and move it so as to bring the water in contact with the gas. (?) *Remove the glass plate before placing the mouth of the bottle under the water.*

Slowly introduce a lighted candle held on a wire into an inverted bottle of the gas, as you did with hydrogen. Does it support combustion? How does it behave on the instant of contact with the candle-flame?

Fill a dry bottle with hydrochloric-acid gas by downward displacement. The gas can be made by gently heating a little strong hydrochloric acid placed in a test-tube with a cork bearing a delivery tube bent downward. Bring

the bottle mouth to mouth with a bottle of ammonia gas. Let the bottles stand until the product has settled on the sides. Scrape some of it out and heat it carefully in a porcelain crucible or on a piece of platinum foil. (?) What is it?

EXPERIMENT 55.—**Ammonium salts.**—Dilute some ammonium hydroxide (ammonia water) with about three times its volume of water in a beaker. How does the liquid affect red and blue litmus paper? Does it act upon the litmus in the same way as caustic soda?

Dilute about 5 c.c. of hydrochloric acid with three times its volume of water in a dish and investigate its behavior with both kinds of litmus paper. *All acids affect litmus paper in the same way as hydrochloric acid.* Ammonium hydroxide and sodium hydroxide are *bases*. *All soluble bases affect litmus paper in the same way.*

Now add your dilute ammonium hydroxide, drop by drop, to the hydrochloric acid in the dish, stirring constantly. From time to time dip small pieces of blue litmus paper into the liquid. When the latter is no longer turned red you will find that a piece of red litmus paper is turned blue. At the same time the liquid acquires a faint odor of ammonia. Why?

Evaporate the liquid in the dish to dryness. Examine the residue. Is it ammonium chloride? Heat some of it on a piece of platinum foil or in a crucible. Write the equation.

Repeat the whole experiment, using nitric acid instead of hydrochloric. Write the equation.

Dissolve some ammonium chloride in water in a test-tube. Add a fragment of sodium hydroxide to the liquid and heat gently. Notice the odor of the gas given off. Hold a fragment of red litmus paper in the gas. Repeat, using potassium hydroxide instead of sodium hydroxide. In the same way investigate the behavior of ammonium

nitrate with sodium hydroxide and potassium hydroxide. Notice that *strong bases liberate ammonia from ammonium salts.* Write equations for the four chemical changes which have taken place.

Study the effect of heat upon small quantities of ammonium nitrate, chloride, and sulphate. Use a porcelain crucible or a piece of platinum foil.

EXPERIMENT 56.—Dilute about 30 c.c. of ammonia with about ten times its volume of water, in a flask. Shake up the liquid with salt until no more dissolves. Fill the apparatus employed in the electrolysis of water (Fig. 6) with the clear liquid and pass the current. What two gases collect? Try to burn each. Close the stop-cocks for a time and ascertain the relative quantities of the gases. If the apparatus is not graduated, measure the length of the columns of gas with a meter scale.

In this experiment the salt is added only to assist in conducting the current through the liquid, and thus make the process more rapid.

QUESTIONS

1. What does the presence of ammonia indicate with regard to the fitness of a sample of water for drinking ?

2. Explain the fact that the air of stables often smells strongly of ammonia.

3. Remembering that the density of nitrogen referred to hydrogen is 14, and that the symbol N means 14 parts of nitrogen by weight, deduce from Experiment 56 the formula of ammonia.

4. Devise two methods of distinguishing an ammonium salt from a sodium or a potassium salt.

5. How would you convert the hydrogen of ammonia into water ?

6. How would you convert the hydrogen of water into ammonia ? (See paragraph 139, Part I.)

7. How would you convert free nitrogen into ammonium nitrate ? (See p. 105, Part I.)

8. What are some of the uses of ammonia water? *Liquid ammonia* is largely employed for one purpose only. What is it?

9. How could you make ammonia, taking the hydrogen from sulphuric acid and the nitrogen from ammonium nitrite, NH_4NO_2?

10. Explain exactly what is meant by a radical.

Problems

47. 856 grams of ammonium chloride are heated with sodium hydroxide. How much ammonia by weight escapes?

48. Calculate the percentage composition of

     a. Ammonium chloride, NH_4Cl.

     b. Ammonium nitrate, NH_4NO_3.

     c. Ammonium sulphate, $(NH_4)_2SO_4$.

     d. Ammonium hydroxide, NH_4OH.

49. When a stream of electric sparks is passed through ammonia it is decomposed, two volumes yielding one volume of nitrogen and three volumes of hydrogen. What volumes of nitrogen and hydrogen are formed when 300 c.c. of ammonia are treated in this way?

50. 100 c.c. of ammonia are decomposed by a stream of sparks. (*a*) What volume of oxygen must be added to the resulting mixture to combine with the hydrogen and produce water? (*b*) After the water has condensed, what gas will remain in the tube, and how much?

51. 32 c.c. of ammonia are decomposed by sparks, 50 c.c. of oxygen are added, and the mixture is caused to explode. What volumes of what gases are left?

52. An unknown volume of ammonia is decomposed in a eudiometer, an unknown volume of oxygen is mixed with it, and the mixture exploded. After the explosion the contraction in volume is 18 c.c. and the tube still contains some oxygen. (*a*) What volume of ammonia was taken in the first place, and (*b*) what volume of nitrogen was left in the tube?

53. Ammonium chloride is heated in a flask with sodium hydroxide and the ammonia passed into 31.5 grams of pure nitric acid. How much ammonium chloride must be used in order to convert all the nitric acid into ammonium nitrate?

CHAPTER XV

COMPOUNDS OF NITROGEN AND OXYGEN

EXPERIMENT 57.—**Nitrous oxide.**—Fill a wide test-tube one-third with ammonium nitrate. Clamp it in an inclined position, and insert a perforated cork with a delivery tube. It is advisable to pass the gas through an empty wide test-tube closed by a doubly perforated cork before collecting it. Apply a gentle heat and collect the gas over warm water. *The evolution of gas must be slow —a bubble or two a second. If it becomes too rapid explosions result.* This can be easily controlled by lowering or removing the flame. Stop heating and remove the cork before the ammonium nitrate is exhausted. *Explosions sometimes occur when the quantity of substance becomes small.* If the ammonium nitrate shows signs of giving out before you have enough gas, disconnect, add more of it directly to the liquid in the test-tube, and resume heating cautiously. Is there evidence of the formation of any product besides the gas? What?

Collect three bottles and two test-tubes full of the gas. Use one bottle to determine color, odor, and taste. (?) Try the spark test in a test-tube. Ascertain if the gas is soluble in water. Plunge a lighted candle into a bottle of it. (?) Set fire to some sulphur in a deflagrating spoon, and *at the instant the sulphur begins to burn* plunge it into the third bottle of nitrous oxide. It should be extinguished. Cover the bottle, and heat the sulphur until it burns vigorously. Plunge it again into the gas. (?) Is nitrous oxide easy or difficult to decompose into its elements? Which has probably the higher temperature, the candle-flame or the flame of burning sulphur?

EXPERIMENT 58.—**Nitric oxide.**—*Make no attempt to ascertain the odor of nitric oxide. It must not be inhaled,*

and experiments with it should be carried out under the hood, if possible. If you do not work under the hood, keep the bottles of the gas covered during combustions and let the products escape out of the windows.

Nitric oxide is made in the same apparatus which is used for generating hydrogen. Fill the generator to the depth of about 1 cm. with copper clippings or cut pieces of sheet copper. In another vessel, dilute some nitric acid with twice its volume of water. Cool this liquid and pour it upon the copper until the generator is one-third filled. Collect the gas over water. It is well to stand the generator in cold water. If the evolution of gas becomes too energetic, pour a little water down the funnel-tube. Collect four bottles and one test-tube of the gas. Then stop, as even the first gas which comes off is not quite pure and the later portions contain large quantities of *nitrous* oxide and other impurities. Leave the bottles standing in the water.

Take the apparatus to the hood, disconnect it (*do not inhale the gas*) and pour a little of the blue liquid into a clean dish. Put a small flame under it and let it evaporate almost to dryness under the hood. What is the product? Wash off the copper in the generator and return what is left of it to the stock-bottle.

Expose a bottle of nitric oxide to the air. (?) Into another bottle slowly admit oxygen from a cylinder or gas holder. Stop after adding a few bubbles of oxygen, and shake the bottle, keeping its mouth under water; then continue adding oxygen. Explain these results.

Slip aside the cover of a third bottle and plunge to the *bottom* of the bottle some sulphur, burning vigorously in a spoon. Remove the sulphur at once, keeping the bottle covered, and do the same thing with a lighted candle. Why should the candle be placed in the bottom of the bottle? Interpret the results.

Into the fourth bottle introduce a piece of burning magnesium held in forceps. (?) Which flame has the higher temperature, that of a candle or magnesium? Which gas requires the higher temperature to decompose it, nitrous or nitric oxide? Construct a tabular view of the properties of the two gases.

EXPERIMENT 59.—**Nitrogen peroxide.**—Place in a dry sealed tube of hard glass lead nitrate to the depth of about 1 cm. and heat gently. The crackling which often occurs is due to the fact that the crystals inclose small drops of water and fly to pieces when this water is vaporized by heat. What two gases are given off? What is left in the tube? Bring into the mouth of the tube a piece of moist blue litmus paper. (?) The result is due to the fact that nitrogen peroxide reacts with water, producing *nitric acid.*

EXPERIMENT 60.—**Formation of nitric acid from water and air under the influence of electric discharges.**—Select a small glass flask or bottle and a 2-hole rubber stopper which fits it. The holes in the stopper should be small. Pass through each hole a platinum wire and jam a piece of glass rod into each hole to fix the position of the wires. Both wires should reach nearly to the bottom of the bottle, and should be bent toward each other so that the ends are less than 1 cm. apart. They must not touch. The bottom of the bottle must be wet. Throw a piece of moist blue litmus paper into the bottle, insert tightly the cork with the wires, and pass a stream of sparks from a coil for half an hour, or until the litmus paper changes color. The result is due to the production of *nitric acid.* What light does this experiment throw upon the presence of nitric acid in rain (paragraph 132, Part I)? Upon the supply of nitrogen to plants?

EXPERIMENT 61.—**Preparation of nitric acid.**—*The gases given off when nitric acid acts upon metals and the vapor of nitric acid itself are poisonous and must*

not be inhaled. Do not get nitric acid upon the skin or clothing.

Fit up the apparatus shown in Fig. 22. Roughly weigh on the platform scales enough potassium nitrate to fill the retort about one-third. Weigh off in a beaker an equal quantity of strong sulphuric acid. Introduce the potassium nitrate into the retort by means of a piece of paper. Add the sulphuric acid, insert the *glass stopper* (not a rubber or wooden cork, which would be rapidly destroyed by the nitric acid) and heat gently.
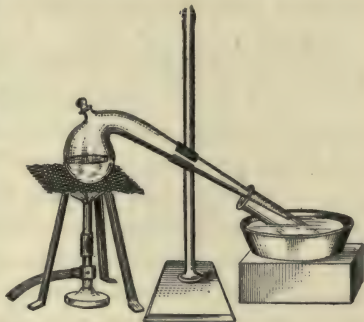
Fig. 22.

Only vapor, not solid or liquid, must pass over. Why?

Examine the nitric acid which collects and record its properties. Use it in the following experiments. Cover a piece of zinc with water in a test-tube and slowly add nitric acid. Do the same thing with a little iron filings and a piece of magnesium. In these reactions water is produced, together with the nitrate of the metal used. The gas produced may be nitrous oxide, nitric oxide, or nitrogen peroxide according to the temperature and strength of the acid. Do not try to write the equations, which are quite difficult. Simply remember the general character of the action and the way in which it differs from the action of sulphuric or hydrochloric acid on the same metals.

Drop a fragment of tin into strong nitric acid in a test-tube. What are the products (paragraph 154, Part I)?

Drop a piece of cork into nitric acid and let it remain

there for a time. Let a drop of nitric acid fall upon a colored fabric of any kind. What is the action of nitric acid upon organic matter? Would the formula of the acid lead you to expect such action?

EXPERIMENT 62.—**Aqua regia.**—Pick up a small piece of gold leaf with the end of a wet glass rod, and rinse it into a test-tube with water. In the same way place another piece of gold-leaf in another test-tube. Add to one tube nitric acid and to the other hydrochloric acid. Heat both tubes. Does the gold dissolve. Pour the contents of either tube into the other, and go on heating. (?) The product is gold chloride, and the gold dissolves because the oxygen of the nitric acid liberates chlorine from the hydrochloric acid and the chlorine attacks the gold. Suggest another substance which could be used with the hydrochloric acid in place of the nitric acid, though not so conveniently. The mixture of nitric and hydrochloric acids will also dissolve platinum.

EXPERIMENT 63.—**The nitrates.**—Examine potassium nitrate and sodium nitrate. Try the solubility of each in water. Place a drop of each solution on a clean glass plate, let it evaporate to dryness, and examine the crystals left with a good lens. Record your observations.

In a small iron or nickel dish melt enough potassium nitrate to half fill it and heat the melted salt with the full power of the burner flame. Be careful not to upset the dish, as the melted substance would burn deeply into the table. Throw into it a piece of charcoal which has been heated at one corner to redness. Stand aside as the melted substance may sputter. Throw a fragment of sulphur into the dish. Is the oxygen of potassium nitrate firmly or loosely held? Does the result throw any light upon the behavior of the potassium nitrate in gunpowder? Weigh out 6 grams of powdered potassium nitrate, 1 gram of powdered charcoal, and 1 gram of flowers of sulphur.

Mix thoroughly by pouring from one paper to another—NOT IN A MORTAR. Place the heap upon a piece of wood, thrust a piece of filter-paper into it, light the paper and stand aside. If the paper fails to ignite the mixture, wait until the last spark of the burning paper is extinguished before approaching the heap to make a second attempt. Explain.

Place a crystal of silver nitrate on charcoal and let the burner flame play upon it. (?)

EXPERIMENT 64.—**The nitrites.**—Examine sodium nitrite. Dissolve some of it in water. Add to a portion of the solution a drop or two of silver nitrate solution. To another portion add carefully a little sulphuric acid. Interpret the result after reading paragraph 159, p. 117, Part I.

QUESTIONS

1. What is the explanation of the peculiar conduct of nitrous and nitric oxides toward combustible substances ?

2. Vitali, an Italian experimenter, plunged cats into nitric oxide, and observed that they died in convulsions. Why is it that this experiment does *not* furnish any information about the action of nitric oxide upon the animal body ?

3. Sodium nitrate is much cheaper than the potassium salt; but supposing that the two sold at the same price, why would it be more profitable to use the sodium compound in making nitric acid ?

4. Why do railroads object to transporting nitric acid if packed in glass vessels ?

5. Describe in general terms the action of nitric acid upon metals, and explain what becomes of the hydrogen of the acid.

6. Nitrous oxide yields the spark test and supports combustion brilliantly. How could it be distinguished from oxygen ?

7. Nitrogen and chlorine do not combine directly to produce nitrogen chloride; but supposing they did, would heat or cold be produced ? Why ?

8. Why is it impossible to employ nitrogen chloride practically as an explosive ?

PROBLEMS

54. What weight of nitric acid containing 80 per cent HNO_3 is necessary to dissolve 10 grams of cupric oxide ?

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O.$$
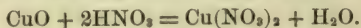
55. What weight of pure nitric acid would contain 50 grams of oxygen ?

56. Assuming that the density of pure nitric acid is 1.5, how much oxygen do 3 liters of it contain ?

57. How much nitric acid can be obtained (a) by heating 200 kilos of sodium nitrate with sulphuric acid; (b) by heating 200 kilos of potassium nitrate with sulphuric acid ?

58. I require 120 grams of cupric oxide. How much crystallized cupric nitrate must be heated to redness to make it ?

$$Cu(NO_3)_2 3H_2O = CuO + 2NO_2 + O + 3H_2O.$$
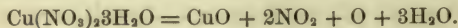
59. How much nitric acid is needed to convert 400 grams of potassium hydroxide into potassium nitrate ?

$$KOH + HNO_3 = KNO_3 + H_2O.$$
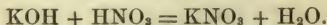
60. Calculate the percentage composition of N_2O_5.

61. Calculate the formula of a compound having the following composition:

> 9.09 per cent nitrogen;
> 20.77 " oxygen;
> 70.13 " silver.

What is the name of the compound and how could you make it ?

CHAPTER XVI

ATOMIC AND MOLECULAR WEIGHTS—AVOGADRO'S RULE

No experiments.

QUESTIONS

Use the utmost precision in answering these questions. The subject is very important.

1. Explain exactly what is meant by the term *molecular weight*.

2. What is the exact difference of meaning between the follow-

ing two formulas—*a.* NO_2; *b.* N_2O_4? Answer this question first in the language of grams and liters. Then answer again in the language of the atomic theory.

3. Why is the density of a gas or vapor referred to hydrogen equal to one half the molecular weight? Answer this question first in the language of grams and liters; then in the language of the atomic theory.

4. Explain how to calculate from the formula the weight of one liter of any gas or vapor.

5. Explain how to calculate from the formula the volume of one gram of any gas or vapor. For what temperature and pressure are the results obtained in 4 and 5 good?

6. Show that 18 grams of water, H_2O,
        58.5 "   " salt, $NaCl$,
        63   "   " nitric acid, HNO_3,
        2   "   " hydrogen, H_2,

must all contain the same number of molecules.

7. Explain Avogadro's Rule.

8. What is the law of simple volume ratios? Why would the atomic theory lead us to expect it to be true?

9. What basis of fact is required in order to double a formula?

PROBLEMS

62. Calculate the molecular weights of the following compounds:

    a. Sugar, $C_{12}H_{22}O_{11}$;
    b. Bismuth nitrate, $Bi(NO_3)_3$;
    c. Nitroglycerin, $C_3H_5(NO_3)_3$;
    d. Glucose, $C_6H_{12}O_6$.

63. What is the weight of 28 liters (*a*) of nitrous oxide? (*b*) of nitric oxide?

64. What is the volume (*a*) of 11 grams of nitrous oxide? (*b*) of 5 grams of nitric oxide?

65. What volume of hydrogen is needed to form water with the oxygen (*a*) of 22 liters of nitrous oxide? (*b*) of 22 grams of nitrous oxide?

$$N_2O + H_2 = H_2O + N_2.$$
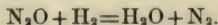
66. What is the volume of 13 grams of nitric oxide?

67. What volume of nitrous oxide—measured at standard con-

ditions—can be made from 80 grams of ammonium nitrate? Solve by inspection.

68. How much ammonium nitrate is needed to make 80 liters of nitrous oxide?

69. How much ammonium nitrate is needed to make 4,000 c.c. of nitrous oxide?

70. How much copper is needed to produce 30 liters of nitric oxide?

71. How much ammonium nitrate is needed to produce 10 liters of nitrous oxide?

72. What volume of nitrous oxide at 15° C. and 700 mm. can be obtained by heating 200 grams of ammonium nitrate?

73. What volume of nitric oxide at 13° and 740 mm. is obtained by dissolving 80 grams of copper in nitric acid?

CHAPTER XVII

ACIDS, BASES, AND SALTS—METALS AND NON-METALS

EXPERIMENT 65.—**The reaction of sodium hydroxide with hydrochloric acid.**—Dissolve a piece of sodium hydroxide about 5 cm. (2 inches) long in 10 c.c. of water in a beaker. Carefully and slowly add strong hydrochloric acid, stirring constantly. Is there evidence of energetic action? A white solid separates. What is it? What else was formed at the same time?

Let the solid settle and pour off the liquid. Dissolve the solid in the smallest possible quantity of water, transfer it to a dish, and evaporate it slowly to dryness. When the residue is perfectly dry, let it cool and examine it. Taste it. (?) Write the equation.

EXPERIMENT 66.—**The reaction of sodium hydroxide with sulphuric acid.**—Make a *little* very strong solution of sodium hydroxide in a test-tube. Place about 2 c.c. of the liquid in another test-tube and clamp it vertically. Drop strong sulphuric acid into it—*one drop at a time*—

from a tube drawn out to a jet. Be careful. The reaction is violent. What are the two products? Is heat evolved or absorbed? Write the equation.

An acid and a base always react, forming a salt and water when they are brought together, but the reaction is not always as energetic as in this instance.

EXPERIMENT 67.—**Properties of acids and bases.**—Prepare very dilute hydrochloric, nitric, sulphuric, and acetic acids by diluting the acids with about 100 times their volume of water. Make at least 300 c.c. of the hydrochloric and nitric: a small quantity only of the others. Taste each of these liquids. Put a drop on red litmus paper. On blue litmus paper. On turmeric paper.

Dilute some ammonia with about 100 volumes of water. Dissolve about 3 grams of sodium hydroxide in 300 c.c. of water. Dissolve 3 grams of potassium hydroxide in 300 c.c. of water. Obtain some clear lime-water—this is already sufficiently dilute. Taste these liquids, rub them between the fingers, and test them with the same papers which were employed for the acids.

EXPERIMENT 68. — **Neutralization.** — (1) Clamp two *burettes* (Fig. 23) vertically side by side. Fill one with dilute hydrochloric acid (from Experiment 67), and let the liquid slowly drop out until the bottom of the meniscus (Fig. 7, Part II) is at O. Fill the other to O with sodium hydroxide solution (from Experiment 67). Measure out 10 c.c. of hydrochloric acid into a clean beaker, and add a few drops of litmus solution—enough to color the liquid *faintly*.

FIG. 23.

Now allow sodium hydroxide solution to run into the liquid, stirring with a glass rod until a change in color occurs. This liquid must fall one drop at a time, and the change in color should be produced by a single drop.

Before this last drop was added the liquid was *acid*—that is, it contained $\overset{+}{H}$ ions; afterward it was *alkaline,* it contained $\overline{OH}$ ions. Read off the level of the liquid in the burette, and calculate how much of your sodium hydroxide would be required for 1 c.c. of your acid.

Now take 20 c.c. of the hydrochloric acid and add, instead of litmus, 2 or 3 drops of a solution of phenol phthalein. The liquid will remain colorless. Stir the liquid constantly and find out just how much of the sodium hydroxide solution is required to make it alkaline. In this case the $\overline{OH}$ ions, when there are any present, will produce a red color.

Take the reading and calculate again how much of the sodium hydroxide is required for 1 c.c. of the acid. Do the two results agree? Repeat until you are sure that there is a fixed relation between the quantities of the two liquids which react.

What becomes of the $\overline{OH}$ ions which are added before the color change occurs?

(2) Repeat, using potassium hydroxide and nitric acid —the dilute liquids from Experiment 67. This time measure off 10 c.c. of the base and add the acid drop by drop from its burette. Use litmus as the indicator. Take 20 c.c. of the base the second time and use a few drops of a solution of *cochineal,* easily made by digesting the crushed insects in alcohol for some hours. It is orange when acid and violet when alkaline.

If time permits, repeat (1), using potassium hydroxide instead of sodium hydroxide with the hydrochloric acid. Calculate the volume of your potassium hydroxide which would be equivalent in neutralizing power to 1 c.c. of your sodium hydroxide. Thus suppose that

8 c.c. NaOH are equivalent to 10 c.c. HCl,
and   12 " KOH   "   "   " 10 " "
clearly 8 " NaOH "   "   " 12 " KOH,
and   1 " NaOH is   "   " $1\frac{2}{8}$, or 1.5 c.c. KOH.

Repeat (2), using sodium hydroxide instead of potassium hydroxide with the nitric acid. Calculate again the volume of your KOH solution, which is equivalent to 1 c.c. of your NaOH. Does the result agree with that obtained above? If not, repeat. Since the burette only reads to 0.1 c.c., do not look for absolute agreement.

EXPERIMENT 69. — **Electrolysis.** — Place some dilute solution of copper sulphate, $CuSO_4$, in a beaker. In the liquid place two pieces of platinum foil each about 2 cm. square. Each is attached to an insulated copper wire which leads to the terminal of an Edison-Lalande cell, or some other source of the electric current. It is well to have a cheap galvanometer in the circuit. Pass the current for fifteen minutes and observe the result. The current evidently passes through the liquid. What carries it? Does the copper go to the negative or positive pole? Why? Reverse the direction of the current for a time. (?) The platinum foil can be cleaned with a little nitric acid.

Dissolve some sugar in about twenty times its weight of distilled water, and introduce the electrodes. A galvanometer must be in the circuit. Does the sugar solution conduct? Sugar contains much hydrogen. Its formula is $C_{12}H_{22}O_{11}$. Is it an acid? Does it yield $\overset{+}{H}$ ions when dissolved in water? Verify your conclusion by testing the solution with red and blue litmus paper.

Dilute some alcohol with about ten times its volume of water and introduce the electrodes. Does it conduct? Alcohol is the hydroxide of a radical. Its formula is C_2H_5OH. Is it a base? Does it dissociate, yielding $O\overset{-}{H}$

ions when mixed with water? Verify your conclusion by testing the liquid with both kinds of litmus paper.

Add very dilute sulphuric acid (about 1 to 100 parts of water) to some blue litmus solution, one drop at a time, stirring constantly until the color is purple, half-way between blue and red. If you put in too much acid, making the color red, add very dilute ammonia. Dissolve some sodium sulphate in water, color the liquid with this neutral litmus, place the liquid in a U-tube, and pass the current for a time. Is any metal deposited at the negative pole? What is formed there? Salts of the metals of the sodium and calcium groups always behave in this way when the current is passed through water solutions. What happens at the positive pole?

EXPERIMENT 70.—**Metals and non-metals.**—As a typical solid non-metal, examine *sulphur*. As a typical metal, examine *lead*. Notice the difference in luster. If the lead is tarnished, scrape it to expose a fresh surface. Rub the sulphur vigorously on the coat-sleeve, and bring it near to some fragments of paper. Notice that it receives a charge and retains it. This shows that the sulphur is a very bad conductor of electricity. Treat the lead in a similar way, and notice that the charge is immediately conducted away through the lead and the body to the earth. The lead *conducts* the current. The same difference exists between the capacity of the two substances for conducting *heat*.

Investigate the tenacity of the two by endeavoring to pull apart a fragment with the hands. (?) Investigate their behavior under the hammer. What are the chief physical differences between metals and non-metals? What are the chemical differences?

As an example of an element on the border-line between the two classes examine *antimony*. Has it a metallic luster? Is it malleable?

Questions

1. What is an acid ? What is a base ? What happens when the two are brought together ? What is a salt ?

2. How do acids act upon oxides ? Upon carbonates ? Why is it that no gas escapes when an acid acts upon an oxide or a hydroxide ?

3. What is an *ion* ? Give two examples of ions which are single atoms. Give two examples of ions which are groups of atoms.

4. What is the exact difference between chlorine ions and chlorine gas ?

5. Sodium, like other metals, contains but a single atom in its molecule. What, then, is the difference between metallic sodium and sodium ions ?

6. According to the idea of electrolytic dissociation, when the substances are all dissolved in water,

Sodium hydroxide consists of $\overset{+}{\text{Na}}$ and $\overset{-}{\text{OH}}$;

Hydrochloric acid   "   " $\overset{+}{\text{H}}$ and $\overset{-}{\text{Cl}}$;

Sodium chloride   "   " $\overset{+}{\text{Na}}$ and $\overset{-}{\text{Cl}}$.

Between what two ions does the actual reaction occur when NaOH and HCl are brought together ? Discuss exactly what happens to all four ions.

7. Using the dissociation-idea, explain the fact that all salts of the same metal when dissolved in abundant water produce the same color.

8. Is electrolytic dissociation a fact or a supposition ?

Problems

74. 10 grams of pure sodium hydroxide are dissolved in water. *a.* How much nitric acid must be added to make the solution neutral ? *b.* How much sodium nitrate would be obtained if this was done ?

75. I have a solution which contains just 40 grams of pure sodium hydroxide in 1 liter. Calculate the quantities by weight of (*a*) HCl, (*b*) HNO_3, and (*c*) H_2SO_4, which will be required to neutralize 1 c.c. of it.

76. 15.75 grams of nitric acid are mixed with 23.25 grams of

sodium hydroxide, both dissolved in water. What two compounds does the solution contain and how much?

77. In ascertaining the strength of a dilute solution of HCl, 50 c.c. of it were measured out and neutralized with a solution of sodium hydroxide containing .003 gram of NaOH in 1 c.c. 40 c.c. of the sodium hydroxide solution was required. What weight of HCl was contained in 1 c.c. of the hydrochloric acid?

78. 30 c.c. of a solution of potassium hydroxide containing .01 gram of KOH in 1 c.c. was needed to neutralize 40 c.c. of a solution of HCl. How much HCl did 15 c.c. of the hydrochloric-acid solution contain?

79. 20 c.c. of a solution containing .005 gram of KOH in 1 c.c. just neutralized 20 c.c. of a solution of hydrochloric acid. How much HCl did 15 c.c. of the latter contain?

CHAPTER XVIII

THE SODIUM GROUP

EXPERIMENT 71.—**Potassium.**—*Potassium is preserved under naphtha, and the bottle containing it must be kept stoppered and not opened in the vicinity of a flame. It catches fire on contact with water, and all apparatus used in handling it, as well as the desk, must be dry. It must not be touched with the fingers. When exposed to the air it takes fire spontaneously after a time; therefore it must not be put away under the desk or left lying around. When thrown into water it reacts explosively, and a glass plate should be used to protect the eyes when the experiment is performed.*

Examine a piece of potassium. Cut it and notice the luster. Is it permanent? Why? Add 2 or 3 drops of a solution of phenol phthalein to a bottle half full of water, and throw in a piece of potassium half the size of a small pea (*no larger*). What happens? What sub-

stances are formed? Does the liquid contain hydroxyl ions?

Scrape a hollow in a fragment of charcoal, place in it a fragment of potassium half the size of a pea, and let the burner flame play upon it. Notice the flame color.

Make in the form of a small table a comparison between potassium and sodium. Include in this comparison luster, permanence of luster, hardness, flame color, behavior with water, and any other properties that may appear important.

EXPERIMENT 72.—**Potassium compounds.**—Examine potassium hydroxide, chloride, chlorate, bromide, and carbonate. Test each for solubility in water. Make the flame test with each, using a clean iron wire, as with sodium. Clean the wire after each test by dipping it in a little hydrochloric acid in a beaker and holding it in the flame.

Make a small quantity of a mixture of potassium and sodium chlorides and apply the flame test to the mixture. Look at the flame of the mixture through blue glass.

Make the flame test with lithium chloride, LiCl. If a spectroscope is available, use it to observe the spectra of potassium, sodium, and lithium chlorides separately.

QUESTIONS

1. What is the connection of potassium with plant life?

2. From the standpoint of electrolytic dissociation, what really happens when potassium acts upon water is that the potassium passes from one condition to another. Explain this statement.

3. From the same standpoint, explain why, if a metal acts violently upon water, we should expect its hydroxide to be a strong base and its salts to be good conductors of the electric current.

PROBLEMS

80. How much potassium is required to liberate from water enough hydrogen to combine with 3 grams of oxygen?

81. What volume of oxygen is needed to combine with the hydrogen given off by the action of 9.75 grams of potassium on water ?

82. How much (*a*) potassium carbonate must be heated with how much (*b*) pure charcoal to produce 9.75 grams of potassium, and (*c*) what volume of carbon monoxide would be liberated ?

$$K_2CO_3 + 2C = 3CO + 2K.$$
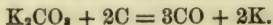
CHAPTER XIX

THE COPPER GROUP

EXPERIMENT 73.—**Copper.**—Examine copper filings and sheet copper. Record its properties. Heat a piece of sheet copper in the Bunsen flame. Place a little copper filings in a test-tube, cover with water, and add hydrochloric acid. Is there any result? Repeat, using water and sulphuric acid. Repeat, using water and nitric acid. What is the gas given off when nitric acid dissolves copper, and why does it turn red on entering the air?

Make a spiral, about 15 cm. long, of copper wire by winding it around a glass tube. Have ready a wide test-tube and a cork to fit it. The test-tube should contain about 1 c.c. of alcohol. Hold the spiral in forceps and pass it through the burner flame until it turns black. (?) Remove it from the flame, place in the test-tube, and loosely cork the latter. When cool, remove it from the tube and examine it. It now has the true color of copper. Explain what has happened.

EXPERIMENT 74.—**Cupric oxide.**—Examine cupric oxide. Mix 3 grams of it with 0.5 gram of powdered charcoal and heat the mixture in a hard glass test-tube with a delivery tube so arranged that any gas given off must pass through lime-water in a wide test-tube. Heat gently at first and then more intensely. When the gas has been

bubbling through the lime-water for a time, introduce a lighted match into the upper part of the wide test-tube. What gas is given off? What must have happened to the copper oxide?

Cover the hard glass tube with a layer of soot from the luminous flame and let it cool completely. Examine the contents with a lens.

How does carbon affect the oxides of most metals? What is the importance of the reaction?

EXPERIMENT 75.—**The effect of cupric oxide upon organic compounds.**—Heat to redness in a hard glass test-tube, 5 grams of a mixture of cupric oxide with $\frac{1}{20}$ of its weight of sugar, both finely powdered and carefully mixed. Conduct the gases given off into the bottom of an empty test-tube which stands in a small beaker containing a freezing mixture. Use a mixture of crushed ice and salt, or else crystallized sodium sulphate with twice its weight of hydrochloric acid. This test-tube is closed with a doubly perforated cork, and from it the gases are led into a second test-tube containing clear lime-water. This tube need not be cooled and must not be corked. What is the result? What does the experiment teach about the composition of sugar? What becomes of the copper oxide? Cover the tube with soot and disconnect before cooling.

EXPERIMENT 76.—**Cupric sulphate. Cupric ions.**—Examine cupric sulphate. Heat a little of it carefully in a porcelain dish. (?) Make a solution of cupric sulphate. What is the color of cupric ions? Place a portion of the solution in a test-tube, add a piece of zinc and a few drops of sulphuric acid to hasten the action. Let stand for some time. The solid product is *copper,* finely divided and lusterless. Why does the liquid lose its color? Which has the strongest tendency to exist as ions, copper or zinc?

Repeat the experiment, using iron (a nail) in place of the zinc.

Place a small piece of clean sheet copper in a solution of silver nitrate. What is the product? Which tends most strongly to exist as ion, copper or silver? What ought, therefore, to be the effect of zinc upon silver nitrate solution? Try it with a fresh portion.

Add a drop or two of your copper sulphate solution to a test-tube half filled with water, and investigate the action of ammonia water on the liquid. This is a delicate test for cupric ions.

QUESTIONS

1. How would you convert cupric ions into metallic copper? Metallic copper into cupric ions?

2. What is the exact difference between cuprous and cupric ions?

3. The same electric current is passed in succession through a solution containing cuprous ions and one containing cupric ions. In one hour .3175 gram of copper deposits in the cupric solution. How much is deposited in the cuprous solution in the same time, and why?

PROBLEM

83. 2 grams of finely divided copper were heated in oxygen. 2.5063 grams of cupric oxide were produced. Calculate the atomic weight of copper.

CHAPTER XX

SILVER

EXPERIMENT 77.—**Silver.**—Dissolve about 0.5 gram of silver nitrate in 50 c.c. of distilled water in a beaker. Try the action of a clean piece of sheet copper upon a portion of the liquid in a test-tube. Add a drop of mercury to another portion. Let both tubes stand some time. The visible product is *silver*. What else must have been produced in both cases?

To the rest of the silver nitrate solution add a solution of sodium chloride. The precipitate is silver chloride, AgCl. Write the equation. In what previous experiment did you make and study silver chloride? What liquid dissolves it? What is the effect of light upon it? Answer these questions from your notes. Stir up the silver chloride with water, allow it to settle, and pour off the water without losing any of the silver chloride. Repeat three or four times. This is called *washing by decantation*. Place a piece of zinc in contact with the silver chloride, and add a drop or two of sulphuric acid. Allow to stand. The product is *silver*. Wash it by decantation, examine it, and record its properties.

EXPERIMENT 78.—**Photography**.—If a negative is available, examine it. What is the material of which the image consists? Describe briefly, from the beginning, the processes through which the negative has passed. Why are the lights and shadows reversed in it? If practicable, expose a piece of sensitive paper back of the negative in a printing-frame to sunlight. The paper must be inserted by dim light, and the sensitive side of the paper must be in contact with the side of the negative bearing the film. Once a minute open *half* the printing-frame in a dim light and examine the progress of the printing. When the print is finished, remove and examine it. How can the unpleasant reddish color be altered? What is *toning*, and how does it affect the chemical composition of the image? Is your picture permanent? Expose it to strong light and find out. If not, how could it be made permanent?

EXPERIMENT 79.—**Silver oxide**.—Add some sodium hydroxide solution to a dilute solution of silver nitrate. The precipitate is silver oxide, Ag_2O. Complete the equation—

$$2AgNO_3 + 2NaOH = Ag_2O + \ldots + \ldots$$
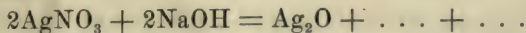
What experiment have you made upon the solubility of

gold? Is it soluble in nitric acid? In hydrochloric acid?
In a mixture of both? How could you separate gold
from silver in an alloy of both metals?

QUESTIONS

1. How could you convert silver nitrate into silver chloride?
Silver chloride into silver nitrate?

2. How could you prepare pure silver from a silver coin con-
taining 90 per cent silver and 10 per cent copper?

PROBLEMS

84. Calculate the percentage composition (a) of silver chloride,
AgCl; (b) of silver sulphide, Ag$_2$S.

85. Calculate the formula of a compound of the following
composition:

Silver 65.45
Sulphur 19.39
Arsenic 15.16

86. When hydrogen is heated with silver chloride silver is
produced:

$$AgCl + H = HCl + Ag.$$
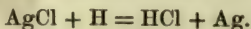
If 52.65 c.c. of hydrogen produce 0.505 gram of silver, what is
the atomic weight of silver?

87. Calculate the percentage composition of silver acetate,
AgC$_2$H$_3$O$_2$.

88. How much zinc is required to precipitate 5 grams of sil-
ver from solution?

$$2\overset{+}{Ag} + Zn = \overset{++}{Zn} + 2Ag.$$
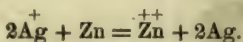
CHAPTER XXI

No experiments.

PROBLEMS

89. How much auric chloride can be made from 65.67 grams
of gold?

90. Calculate the formula of a compound containing 92.3 per
cent of gold and 7.7 per cent of oxygen.

91. What volume of oxygen is produced when 49 grams of auric oxide are heated ?

CHAPTER XXII

THE CALCIUM GROUP

EXPERIMENT 80.—**Calcium compounds.**—Support a piece of marble on a pipe-stem triangle and heat it with the flame of a blast-lamp for fifteen minutes. Examine the product. Is the change complete or partial? What gas has escaped? In what respects would the result have been different if you had heated the marble in a sealed vessel? Write the equation.

Place the mass in a beaker containing distilled water, allow it to stand for a time, and remove the unchanged marble. Decant the liquid carefully upon a filter. What is the name and formula of the white solid which is left? The liquid which runs through the filter is *lime-water*. Test its action upon red and blue litmus paper. Dissolve a little *ammonium oxalate* in distilled water and add it to some of the lime-water. The precipitate is calcium oxalate. This is a delicate test for calcium. Test faucet water carefully for calcium in the same way.

EXPERIMENT 81.—Examine calcium chloride. Expose a fragment to the air on a dry glass plate for an hour. (?) What is it used for in the laboratory? Make the flame test with it. Make the flame test with strontium chloride and barium chloride. (If the chlorates are at hand, use them instead of the chlorides. The result is more satisfactory.)

Make a very dilute solution of barium chloride, and add to it a few drops of sulphuric acid. The precipitate is *barium sulphate*, $BaSO_4$. This is a delicate test for $\overset{++}{Ba}$ ions, and conversely, a solution of barium chloride is a

delicate test for $\overline{SO}_4$ ions; that is, for sulphuric acid or sulphates.

Divide the liquid containing the precipitate into two parts, and show that the latter is insoluble in hydrochloric acid and in ammonia water. This serves to distinguish barium sulphate from other precipitates of similar appearance.

PROBLEMS

92. A piece of pure marble weighing 10 grams is heated to complete decomposition. (*a*) What is the formula and weight of the substance which remains? (*b*) What gas escapes, and what volume measured at 20° and 740 mm.?

93. How many tons of limestone must be heated to make 200 tons of lime?

94. 1.363 kilos of marble are heated until entirely decomposed, and water is thrown on the residue.

95. Calculate the percentage composition (*a*) of barium sulphate, $BaSO_4$; (*b*) of barium carbonate, $BaCO_3$.

96. 10 grams of barium carbonate are dissolved in hydrochloric acid. (*a*) What volume of carbon dioxide is produced, and (*b*) how much crystallized barium chloride ($BaCl_2 2H_2O$) can be obtained from the solution?

97. How much barium sulphate can be made from 2 grams of calcium sulphate ($CaSO_4$)?

98. 1.182 grams of barium carbonate were dissolved in hydrochloric acid, and the solution precipitated with sulphuric acid. The barium sulphate obtained weighed 1.398 grams. Calculate the percentage of barium in the barium carbonate.

CHAPTER XXIII

MAGNESIUM

EXPERIMENT 82.—Examine *magnesium*. Is it light or heavy? Is its luster affected by the air? Hold a piece of magnesium ribbon 20 cm. (8 in.) long in forceps,

and burn it. Receive the product in a dish and reserve it. Burn a similar piece in steam, proceeding exactly as directed on page 173, Part I. Before introducing the magnesium, show that all the air has been expelled from the beaker by introducing a burning match or candle, which should be extinguished. Compare the products of burning magnesium in air and in steam. Are they identical? Investigate the action of hydrochloric, nitric, and sulphuric acids separately in magnesium. Cover a small piece of the metal with water in a test-tube, and add the acid gradually. Record the results. Remembering that magnesium is bivalent, write the equations for the action of hydrochloric and sulphuric acids upon it. The action of nitric acid is more complicated.

EXPERIMENT 83.—Carefully mix *on paper* 1 gram of powdered magnesium with 1.5 grams of powdered potassium chlorate. The materials must not be ground together. Place the mixture on a brick or a block of wood under the hood, stick a piece of filter paper about 10 cm. long in the heap, light the end of the paper farthest from the powder, and step aside. The action is explosive and the light intense. *If the burning paper fails to ignite the mixture, wait till you are absolutely sure that it is extinguished before approaching.*

What are the products of the change? Why is the action so rapid? What application is made of mixtures of magnesium with substances yielding oxygen?

QUESTIONS

1. What is the valence of magnesium in $MgCl_2$, MgO, $MgSO_4$, and $Mg(NO_3)_2$? Why?

2. What is the chemical formula of calcined magnesia? of Epsom salts? Why is magnesium chloride objectionable in water for steam boilers?

29

3. Can you perceive any connection between the properties of magnesium oxide (almost infusible and non-volatile) and the great brightness of the flame of burning magnesium?

PROBLEMS

99. What volume of oxygen is needed to burn 9 grams of magnesium?

100. If 0.4 gram of magnesium liberated 391 c.c. of dry hydrogen at 13° when treated with HCl, what is the atomic weight of magnesium?

101. The electric current is passed through fused magnesium chloride until 14 grams of magnesium are obtained. What volume of chlorine at standard conditions is liberated?

CHAPTER XXIV

ZINC AND CADMIUM

EXPERIMENT 84.—Examine sheet *zinc* and record its properties. Refer to your notes of former experiments for data regarding the action of acids upon it. Heat a small piece of zinc upon charcoal with the blowpipe flame. Practise with the blowpipe until you can produce a continuous flame. The blast comes from the cheeks, not from the lungs, and the cheeks are refilled with air at intervals without interrupting the flame. What is the deposit upon the charcoal? Repeat Experiment 83, using zinc dust with the $KClO_3$ instead of magnesium. *Care.*

EXPERIMENT 85.—**Quantitative experiment. Atomic weight of zinc.**—Fit up the apparatus shown in Fig. 24. T is a graduated tube holding 100 c.c. It is filled with water, inverted in a vessel of water, and clamped. The flask, F, contains a piece of pure granulated zinc, which has been accurately weighed. It must not weigh more than 0.2 gram. A small piece of platinum wire is wound

around it to hasten the solution of the zinc. Before placing *D* under *T*, the doubly bored rubber cork should
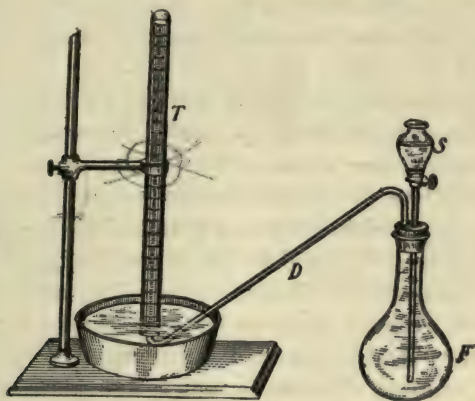
Fig. 24.

be twisted tightly into the flask, the end of *D* placed under water, and *F* and *D* filled with water by pouring water into the separating funnel *S*.

The stop-cock is then closed and the funnel filled with warm (*not hot*) dilute sulphuric acid, one part to three of water. *Remember the precautions necessary in diluting sulphuric acid.* The acid is cautiously allowed to run into *F*, and more of it admitted at intervals until the zinc is *completely dissolved.* The funnel must never become empty, or gas will escape. Remove *D*, cover the open end of *T* with the thumb, and transfer it to a cylinder of water which has had time to acquire the temperature of the laboratory. Clamp the tube so that the level of water inside and out is the same, place a thermometer in the water, and let the apparatus stand 15 minutes. Read the volume of the gas, the temperature, and the atmospheric pressure on the barometer in the laboratory. Record the readings, and repeat them. Take up the different steps of the calculation in the following order:

1. Find the volume your gas would occupy at 0°, 760 mm., and completely *dry*. The method of making the calculation is explained in the Appendix, and is the same that you employed in calculating the weight of a liter of oxygen (p. 38).

2. Calculate the weight of this gas by multiplying the corrected volume in *liters* by 0.0896, the weight of a liter of hydrogen under standard conditions.

3. Calculate by proportion the weight of zinc which would be required to set free 2 grams of hydrogen. Since zinc is bivalent, this will be the atomic weight of zinc.

EXPERIMENT 86.—Examine *cadmium,* and record its properties. Has it the same luster as zinc? Is it denser or lighter? Heat a chip of it on charcoal. (?) Dissolve a little cadmium chloride in water, and place a piece of zinc in the liquid. Allow to stand. What happens? Which of the two metals has the strongest tendency to exist as ions?

PROBLEMS

102. If 0.5 gram of zinc when dissolved in hydrochloric acid set free 183.7 c.c. of hydrogen measured over water at 15° and 760 mm., what is the atomic weight of zinc ?

103. If 1 gram of zinc set free 366 c.c. of hydrogen measured over water at 9° and 748 mm., what is the atomic weight of zinc ?

CHAPTER XXV

MERCURY

Mercury should not be brought into contact with jewelry. Rings should be removed before working with it.

EXPERIMENT 87.—Examine mercury. Is its luster affected by the air? Notice the high density (13.6). Place an iron nail and a fragment of marble upon the

surface of mercury in a beaker. Is there any other element which is a liquid at ordinary temperatures?

Heat a drop of it in a dry, clean test-tube, and describe the result. Incline the tube when introducing the metal, or the shock may break the tube.

Place a drop of mercury in a watch-glass and rub it upon a piece of clean copper. (?) What is an amalgam? Heat the copper carefully. (?)

Try the action of dilute hydrochloric, sulphuric, and nitric acids upon small drops of the metal.

Mercury must not be thrown into the sinks.

EXPERIMENT 88.—Place some mercuric sulphide, HgS, in a short tube about 0.5 cm. wide, open at both ends, and gently heat the portion containing the substance, inclining the tube so that a current of hot air shall be drawn over the mercuric sulphide. Describe and explain the result. Write the equation. Is this the usual effect of heating with abundant air-supply upon sulphides? What other sulphides might be expected to behave like mercuric sulphide under the same circumstances?

EXPERIMENT 89.—**Mercurous compounds.**—Add hydrochloric acid, drop by drop, to a solution of mercurous nitrate. The visible product is mercurous chloride. Does it look like silver chloride? Treat it with ammonia water. Does it behave like silver chloride with ammonia?

EXPERIMENT 90. — **Mercuric compounds.** — *Mercuric chloride is intensely poisonous. It must not be touched with the fingers.* Dissolve a little mercuric chloride in about 50 c.c. of water. To a portion of the solution add a solution of sodium hydroxide. The precipitate is mercuric oxide, HgO—yellow because it is finely divided. Complete the equation—

$$HgCl_2 + 2NaOH =$$
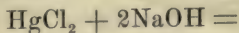
To another portion of the solution add a solution of potassium iodide, one drop at a time, shaking constantly.

The precipitate is mercuric iodide. Notice that the yellow modification forms first, and immediately passes into the red stable modification. Write the equation. Show that the precipitate is soluble in more potassium iodide solution.

To the rest of the solution add an equal volume of a solution of stannous chloride, $SnCl_2$, and heat the liquid. Explain.

QUESTION

Make a tabular statement of the differences between mercurous and mercuric chlorides, using your experiments and the text of Part I as sources of information.

PROBLEMS

104. 758 grams of mercuric chloride are dissolved in water. (a) How much potassium iodide must be added to the liquid, and (b) how much mercuric iodide will be obtained?

105. If mercurous chloride contains 84.93 per cent mercury and 15.07 per cent chlorine, and if the formula is Hg_2Cl_2, what is the atomic weight of mercury?

106. If mercuric chloride has the formula $HgCl_2$ and contains 73.8 per cent of mercury and 26.2 per cent of chlorine, what is the atomic weight of mercury?

107. 88.5832 grams of mercuric sulphide, when completely decomposed, yield 76.3725 grams of mercury. What is the atomic weight of mercury?

CHAPTER XXVI

BORON AND ALUMINIUM

EXPERIMENT 91.—**Boric acid and borax.**—Dissolve about 10 grams of powdered borax in 50 c.c. of hot water in a beaker. Add 25–30 drops of strong sulphuric acid, and allow to cool. Boric acid, $B(OH)_3$, crystallizes.

Examine boric acid from the stock bottle. Hold a

fragment of it in the Bunsen flame. The flame color can be used as a test for boric acid. Place a little borax (0.2 gram or less) in a dish and moisten it with strong sulphuric acid. Stir with a glass rod, add 5 c.c. of alcohol, and stir again. Set fire to the mixture. Record the result.

Make a little loop in the end of a piece of platinum wire, heat the loop red hot, and dip it into a little borax. Put the wire with the borax which adheres to it back into the flame. What is the cause of the swelling up of the borax? What is the name and composition of the transparent bead which remains?

Heat the bead, and cause a minute quantity of *manganese dioxide* to adhere to it. Melt the bead again, and let it cool. The color is characteristic of *manganese*. Slowly turn the cap at the base of the burner until a small portion of the flame is faintly luminous, and hold the bead in this portion steadily. When cold it should be colorless. Heat it in the outer portion of the flame to restore the color.

Remove the bead by dipping it while hot into cold water and scraping it off, and repeat this experiment, using the blowpipe instead of the burner flame. Use a blowpipe-tip on your burner, closing the holes at the base. The *oxidizing flame* of the blowpipe should be used for making the borax bead, containing the manganese. This flame corresponds to the outer non-luminous portion of the Bunsen-burner flame.

The oxidizing flame is produced by placing the end of the blowpipe nearly in the middle of the flame and blowing steadily. The flame should be blue, *perfectly noiseless,* and parallel to the slit in the burner-tip.

The *reducing flame* should be used to decolorize the manganese borax bead. To produce it, place the tip of the blowpipe at the edge of the flame, and use a more

gentle current of air than that used for the oxidizing flame. The flame will be partly blue and partly yellow. It must be noiseless and steady. It should surround the bead completely, so as to prevent the access of air.

Remove the bead. Make a fresh one, and investigate the color produced in it by a minute fragment of *copper sulphate* in both the outer and inner flames. Record the result.

Make another bead, take up with it a scarcely visible speck of *cobalt nitrate,* and study the color produced.

What use can be made of these phenomena in testing for the metals?

EXPERIMENT 92.—**Aluminium.**—Examine sheet aluminium. Is it affected by the air? How does its density compare with that of familiar metals, like iron and copper? How do small pieces of it behave with *dilute* sulphuric, nitric, and hydrochloric acids? Try each acid separately. What gas is given off? What is the action of a solution of sodium hydroxide on a piece of aluminium?

Examine aluminium powder. This is the "bronze paint" used for mail boxes. Place a heap of it 1 cm. wide on an asbestos plate, and set fire to it. What effect has aluminium upon metallic oxides at high temperatures, and what use is made of the fact?

EXPERIMENT 93.—**Alum.**—Dissolve 10 grams of *aluminium sulphate* in a *little* hot water. In another beaker dissolve 5 grams of *potassium sulphate* in a small quantity of hot water. Both liquids must be clear. If not, decant or filter. Mix the liquids in a glass dish or large beaker, and allow to cool. The product is *potassium-alum.* Place some of the crystals on a glass plate, and examine them with a lens.

QUESTIONS

1. What are some of the uses of aluminium?
2. Why are there so many different alums? What chemical

composition must a substance have in order to be called an alum ?

3. Why is boron considered a non-metal and aluminium a metal ?

PROBLEMS

108. Calculate the percentage composition of borax, $Na_2B_4O_7$-$10H_2O$. Calculate *water*, not hydrogen.

109. What is the formula of a substance containing 31.19 per cent boron and 68.81 per cent oxygen ?

110. If 6.75 grams of aluminium, when dissolved in hydrochloric acid, yield 8.4 liters of hydrogen, what is the atomic weight of the metal ?

CHAPTER XXVII

SILICON

EXPERIMENT 94.—**Hydrogen silicide.**—Double a piece of magnesium ribbon 6 cm. long, and heat it in a sealed tube of hard glass to a bright-red heat for several minutes. Allow to cool, break open the tube, discard the magnesium if any remains, and throw the blackened fragments of glass into dilute hydrochloric acid, 1 part to 2 parts of water, in a beaker. The magnesium produces *magnesium silicide*, $SiMg_2$, with the SiO_2 of the glass. This liberates hydrogen silicide with the acid. Write all the reactions, and explain the cause of the spontaneous ignition of the gas.

EXPERIMENT 95.—Add strong hydrochloric acid to a solution of sodium silicate in a porcelain dish. What is the composition of the jelly which separates? Evaporate slowly to dryness under the hood, allow to cool, moisten the residue with hydrochloric acid, half fill the dish with water, heat to boiling, and filter. The substance left on the filter is *silicon oxide,* SiO_2. Wash it with water until a few drops of the liquid which runs through gives no

precipitate when collected in a test-tube, and mixed with a drop of silver nitrate solution.

Examine some crystals of quartz. Make a drawing of one in your note-book. Can you scratch quartz with a knife? With a file? Is a quartz crystal hard enough to scratch glass?

QUESTIONS

1. In what respect are silicic acid and nitrous acid similar ?
2. What is meant by the term *silicate ?*

PROBLEMS

111. What is the weight of 2.8 liters of hydrogen silicide under standard conditions ?

112. Calculate the formula of a silicate which was found by analysis to possess the following composition :

Zinc	58.6 per cent.
Silicon	12.7 "
Oxygen	28.7 "

CHAPTER XXVIII

TIN

EXPERIMENT 96.—Examine tin-foil, bar tin, and granulated tin, and record the properties of the metal. Are ordinary " tin " vessels made of solid tin? Investigate this by bringing a magnet in contact with a tin vessel of any kind. Tin is not attracted by the magnet. Try this with tin-foil.

Study the effect of heat upon tin by placing some tin-foil in a hollow scraped in a piece of charcoal and letting the blowpipe flame play upon it. Does it melt? Does it absorb oxygen? Place a drop of mercury in a watch-glass and press some tin-foil beneath the surface. What is the product?

EXPERIMENT 97.—Heat some tin-foil under the hood for some time with strong hydrochloric acid in a wide test-tube. The result is a solution of stannous chloride, $SnCl_2$. Dilute the liquid, and place a piece of zinc in it. The product is *tin*. Describe it, and notice that a finely divided metal may have a very different appearance from the compact substance. Have you noticed any other examples of this fact?

EXPERIMENT 98.—**The atomic weight of tin.**—Clean carefully a porcelain crucible, dry and weigh it. Place a little granulated tin in it and weigh again to ascertain the amount of tin taken. This should be from 0.5 to 0.7 gram. The quantity must be accurately known. Cover the bottom of the crucible with water and slowly add nitric acid until the tin is covered. Support the crucible on a pipe-stem triangle, and place a small flame 5 cm. below the bottom. This should be done under the hood. When the action seems complete, evaporate cautiously to dryness, avoiding any spattering which will cause loss of substance and make it necessary to go back to the beginning. When the residue is dry, heat it, gradually at first, and finally intensely; let it cool, and weigh it. There will be a gain in weight, which is due to the fact that the tin now exists as SnO_2. Calculate the atomic weight of tin thus—

Gain in weight : O_2 = weight of tin : x.

For example:

Weight of crucible + tin 16.642
Weight of crucible, empty 14.642

Weight of tin 2.000

Weight of crucible + SnO_2 . . . . 17.180
Weight of crucible + tin 16.642

Increase due to oxygen 538

$$0.538 : 32 = 2 : x.$$
$$x = 119.$$

QUESTIONS

1. Discuss the properties of gray tin and its relations to ordinary tin.

2. If 20° is the temperature at which gray tin and white tin are in equilibrium, what is the condition of the tin of a roof on a winter day? How is it that tin can be used for any purpose requiring exposure to cold?

PROBLEM

113. 1 gram of tin was treated with nitric acid. After evaporation to dryness and heating, the gain in weight was 0.271 gram. Calculate the atomic weight of tin.

CHAPTER XXIX

LEAD

EXPERIMENT 99.—Examine *lead*. Cut a chip off a piece in order to observe the luster of the untarnished metal. Heat a little granulated lead in a test-tube with dilute nitric acid. The product is *lead nitrate*. Examine *litharge,* PbO, and heat a little of it on charcoal with the blowpipe flame. Describe and explain the result. Examine *lead dioxide,* PbO_2. Heat a little of it in a tube sealed at one end (hard glass). Apply the spark test to the gas given off. What is the residue? Examine *red lead*. Treat it with dilute nitric acid. What is the cause of the color-change?

EXPERIMENT 100.—Dissolve about 5 grams of lead nitrate in 100 c.c. of water. Use small portions of this liquid to study the behavior of lead salts with the following substances:

Product.

Sulphuric acid, H_2SO_4 . . . . Lead sulphate, $PbSO_4$
Potassium chromate, K_2CrO_4 Lead chromate (chrome yellow), $PbCrO_4$
Hydrogen sulphide, H_2S . . Lead sulphide, PbS

Write all the equations. In the remainder of the lead nitrate solution place a piece of zinc, and allow it to remain undisturbed as long as possible. The product is *lead*.

QUESTIONS

1. What is the effect of the continual absorption of small quantities of lead upon the body, and what are the antidotes?

2. What is the valence of lead in PbO, $PbCl_2$, PbS, $Pb(NO_3)_2$, and PbO_2?

PROBLEMS

114. If 50 grams of litharge (PbO) contain 3.5862 grams of oxygen, what is the atomic weight of lead?

115. What are the name and formula of a compound of the following composition?

Lead...........................	77.52	per cent.
Carbon........................	4.49	"
Oxygen	17.98	"

CHAPTERS XXX AND XXXI

No experiments.

QUESTIONS

1. What reasons have we for the belief that red and colorless phosphorus are two forms of the same element?

2. Discuss the luminosity of colorless phosphorus. How is the luminosity affected by the composition of the gas in contact with the substance?

PROBLEMS

116. How many liters of oxygen are needed to burn 93 grams of phosphorus to P_2O_5?

117. 20 grams of phosphorus are burned in a vessel from which nothing is allowed to escape. How much will the vessel increase in weight?

118. What volume of air is needed to burn 124 grams of

phosphorus to P_2O_5? Assume that air contains 21 per cent by volume of oxygen.

119. If 4 grams of phosphorus when burned yield 9.16 grams of P_2O_5, what is the atomic weight of phosphorus?

CHAPTERS XXXII AND XXXIII

ARSENIC AND ANTIMONY

EXPERIMENT 101.—**Arsenic.**—Examine the element and record its properties. Heat a fragment of it in a tube of hard glass, closed at one end. Does it melt? Does it vaporize? The two sublimates (steel-gray and black) are different allotropic forms of arsenic. Heat a fragment of arsenic the size of the head of a pin on charcoal with the blowpipe flame. The product is *arsenious oxide*.

EXPERIMENT 102.—*Arsenious oxide.*—Examine the substance and compare it with the *element* arsenic. Heat a trace of arsenious oxide in a sealed tube. (?) Examine the sublimate with a lens. What is the shape of the crystals?

Dissolve about 0.1 gram of arsenious oxide by boiling it gently in a test-tube with dilute hydrochloric acid. Dilute the liquid to 100 c.c. Into a portion of this liquid pass hydrogen sulphide gas—*a slow succession of bubbles.* Use a Kipp generator as a source of the gas, or generate it in a wide test-tube, as directed in Experiment 110. *Work under the hood, and do not inhale the hydrogen sulphide.* Describe what takes place, and write the equation.

Place a clean piece of sheet copper about 2 cm. square in a dish, fill the dish with water, add about 1 c.c. of hydrochloric acid, and heat almost to boiling. Is there any action? Add 1 c.c. of your arsenic solution to the

liquid, and continue heating for ten minutes. The deposit on the copper is *arsenic*. Remove the copper, dry it carefully with filter paper, roll it up, and place it in a tube of hard glass, ·sealed at one end. Heat it gently. (?) Look for a sublimate with a lens.

Mix about 0.1 gram of arsenious oxide with twice its weight of powdered charcoal, and heat the mixture in a tube of hard glass, sealed at one end. Introduce the mixture with a paper trough. The upper part of the tube must be *clean*. Describe and explain the result.

EXPERIMENT 103.—**Antimony.**—Examine the element. Is it a metal? How does it behave under the hammer? Heat a fragment on charcoal with the blowpipe. The product is *antimonious oxide,* Sb_4O_6. Let the globule of melted antimony fall while still red hot on a sheet of paper. (?)

QUESTION

Explain in detail what is meant by the statement that arsenic and antimony stand on the border-line between metals and non-metals. Consider both physical and chemical properties in your answer.

PROBLEMS

120. How much charcoal must be used to reduce 132 grams of arsenious oxide? What volume of carbon monoxide will be given off?

$$As_4O_6 + 6C = 6CO + As_4.$$
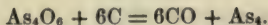
121. In a case of poisoning the arsenic from the body was converted into arsenious sulphide, As_2S_3, and weighed. The weight of the As_2S_3 was 0.82 gram. What quantity of arsenious oxide had been administered?

122. What is the weight of 5.6 liters of arsine at 0° and 760 mm.?

123. Calculate the formula of a compound of the following composition :

Arsenic	48.39 per cent.
Sulphur	51.61 "

CHAPTER XXXIV

CHROMIUM

Experiment 104.—Chrome alum. Preparation of potassium chromate, K_2CrO_4.—Examine chrome alum. What is the form of the crystals? Powder a little. With a portion of the powder try the solubility in water. What is the color of the liquid? Chrome alum contains *chromium sulphate*, $Cr_2(SO_4)_3$, and in it and the other chromium *salts* chromium plays the chemical *rôle* of a trivalent metal, like aluminium.

Mix the rest of the powdered chrome alum with potassium nitrate and potassium carbonate in a clean mortar. The mixture should contain equal quantities of the three substances. Fuse the mixture on a piece of platinum foil, held in forceps. Notice the color of the melted substance. It now contains *potassium chromate*, K_2CrO_4, in which the chromium plays the *rôle* of a non-metal, like sulphur.

Dissolve the melted substance in water and carefully add acetic acid until litmus paper is turned red. Notice the color of the liquid. It is due to the negative ion $\overset{-\,-}{CrO_4}$. What color did positive ions $\overset{+++}{Cr}$ give to water when you dissolved chrome alum in it? Divide the liquid into two portions. To half of it add solution of lead nitrate. Complete the equation—

$$K_2CrO_4 + Pb(NO_3)_2 = PbCrO_4 +$$
<div align="right">Lead chromate</div>
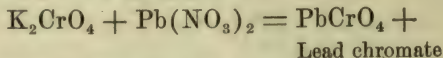
To the rest of the liquid add either nitric or sulphuric acid, drop by drop, until the yellow changes to red. The red liquid contains *potassium dichromate*, $K_2Cr_2O_7$. Complete the equation—

$$2K_2CrO_4 + 2HNO_3 = K_2Cr_2O_7 + \ldots + \ldots$$
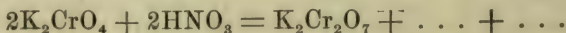
EXPERIMENT 105.—**Preparation of potassium chromate from potassium dichromate.**—Dissolve 5 grams of potassium dichromate in water in a porcelain dish. Add a solution of potassium hydroxide until the liquid is yellow. Evaporate to small volume and let the solution crystallize. The product is *potassium chromate*. Complete the equation—

$$K_2Cr_2O_7 + 2KOH = \ldots + \ldots$$
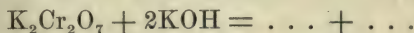
EXPERIMENT 106.—**Preparation of chromic chloride from potassium chromate.**—Powder a *little* potassium chromate, and heat it gently in a test-tube under the hood with strong hydrochloric acid. What gas escapes? What is the change in the color of the liquid? It now contains *chromic chloride,* $CrCl_3$, in which chromium acts like a metal, chemically. Supply the lacking numbers in the equation—

$$K_2CrO_4 + 8HCl = CrCl_3 + KCl + Cl + H_2O$$
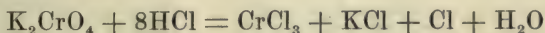
QUESTIONS

1. Briefly state the steps by which you have transformed a chromic salt into a chromate. A chromate into a chromic salt.

2. How can potassium chromate be converted into potassium dichromate? Potassium dichromate into potassium chromate?

PROBLEM

124. Calculate the percentage composition of *chromite,* Cr_2O_3FeO.

CHAPTER XXXV

SULPHUR

EXPERIMENT 107.—**Different forms of sulphur.**—Examine *roll sulphur.* Is it brittle or malleable? dense or light? Rub a piece on the coat-sleeve and bring it near

small pieces of paper. Does it conduct electricity? Hold a piece firmly in the hand close to the ear and notice the crackling noise caused by the portions of sulphur next the hand, expanding as they become warm and cracking away from the other portions, which remain cold. This shows that it is a bad conductor of heat.

Examine *flowers of sulphur,* and record its properties. Powder about 2 grams of roll sulphur and shake it up with 3–5 c.c. carbon disulphide in a dry test-tube. *Caution: Keep the carbon disulphide bottle corked, and avoid the vicinity of flame.* When the sulphur has dissolved, pour the liquid into a dish and let it evaporate spontaneously. Examine the crystals with a lens. They consist of *a-sulphur.*

Fill the smallest size Hessian crucible with crushed roll sulphur, place it in a ring of your stand, and apply heat until the sulphur has melted. Allow to cool. Just when the surface begins to solidify take the crucible in forceps and pour out the liquid portion into a pan of water. Let it cool, and examine the interior. It is covered with crystals of β-sulphur. Make a drawing of a mass of the crystals. Record their properties. Notice that they are different in color as well as shape from the crystals of *a*-sulphur. Preserve some crystals overnight and explain the change which takes place.

When roll sulphur is first made, does it consist of *a*-sulphur or β-sulphur? Which does it consist of after being preserved for a time?

In what respects does the change of *a*-sulphur into β-sulphur by heat (p. 236, Part I) resemble, and in what respects differ, from the change of ice into water?

EXPERIMENT 108.—**Fusion of sulphur. Soft sulphur.** —Fill a wide test-tube about one-quarter with crushed roll sulphur, hold it with a paper holder, and heat slowly. Obtain the three states of fusion described on page 235,

Part I. The three conditions should be perfectly distinct. Let the sulphur in the second liquid stage cool slowly, and note that it passes through the changes in the reverse order.

Now heat the sulphur until it boils vigorously, and pour the liquid in a thin stream into a bottle of cold water, lighting the sulphur vapor at the mouth of the tube while pouring. Examine the product and describe it. Preserve some of it. (?) Is it a stable condition of sulphur?

EXPERIMENT ·109.—**Union of sulphur with metals.**— Fill the same test-tube one-quarter with sulphur, and heat to boiling. Into the tube throw a little powdered iron. (?) Straighten a thin iron wire, heat one end of it to redness, and quickly place it in the sulphur vapor. Cut a thin strip of copper and hold it in the tube.

How does sulphur behave with metals? What is a *sulphide*?

EXPERIMENT 110.—**Hydrogen sulphide.**—*Use the hood. Hydrogen sulphide is poisonous, and must not be inhaled.* Cover the bottom of a gas-generating bottle like the one used in making hydrogen with lumps of *iron sulphide,* FeS. Incline the bottle, and slide the solid in slowly. Cover with water, and add hydrochloric acid through the funnel-tube. Collect several wide test-tubes full of the gas over water as warm as you can work with. (Why is it necessary to use *warm* water?) Cork one of the test-tubes, transfer it to a pan of cold water, remove the cork, and shake the tube, keeping its mouth under water. Is the gas soluble in water? With another test-tube try its combustibility. Meanwhile, allow the hydrogen sulphide to bubble through a bottle or beaker containing at least $\frac{1}{2}$ liter of cold water. Hold the exit tube of your apparatus near a silver coin. A clean piece of sheet copper. A paper wet with a solution of lead acetate. Record and explain the results.

Put the exit tube back in the water and continue passing the gas through for ten minutes. Meanwhile, prepare very dilute solutions of copper sulphate, lead nitrate, cadmium chloride, tartar emetic (an antimony compound), and sodium chloride. Stop the production of the gas by filling the bottle with water and pouring away the liquid. Has the water in the beaker the odor of the gas? Use it to study the effect of hydrogen sulphide upon the solutions you have prepared. Complete the equations:

$$CdCl_2 + H_2S = CdS +$$
$$Pb(NO_3)_2 + H_2S = PbS +$$
$$CuSO_4 + H_2S = CuS +$$
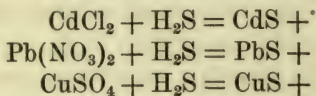
Does the hydrogen sulphide affect the sodium chloride solution? Other metals—e. g., potassium, calcium, and magnesium—behave like sodium. How could you separate one of these metals from lead, cadmium, or copper?

QUESTIONS

1. What is the natural state of sulphur at ordinary temperatures? At 100°? Give facts to support your answer.

2. Why is hydrogen sulphide so much used in analytical chemistry?

PROBLEMS

125. 2 grams of crystallized copper sulphate ($CuSO_45H_2O$) are dissolved in water, and it is required to precipitate all the copper as CuS. How much iron sulphide, and how much hydrochloric acid containing 25 per cent HCl, are needed to generate enough H_2S for the purpose?

126. (a) What volume of hydrogen sulphide is produced when 17.6 grams of FeS are dissolved in HCl? (b) From what weight of mercuric chloride dissolved in water will this quantity of H_2S precipitate the mercury as mercuric sulphide?

$$HgCl_2 + H_2S = HgS + 2HCl.$$
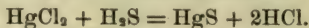
127. What volume of air is needed to burn 500 grams of sulphur to SO_2? Assume that air contains 21 per cent of oxygen by volume.

128. What volume of H_2S escapes when 5 grams of iron sulphide are dissolved in HCl?

129. How much iron sulphide is needed to make 50 liters of H_2S?

In working with sulphur dioxide, use the hood. The gas is irritating, and must not be inhaled.

EXPERIMENT 111.—**Sulphur dioxide, SO_2.**—Fill a small flask one-third with a strong solution of *sodium acid sulphite,* $NaHSO_3$, and allow strong sulphuric acid to drop slowly into it from a separating funnel which passes through one hole in the cork. Lead away the SO_2 by a tube passing through the other hole, and collect it by downward displacement in dry, covered vessels. Collect two wide test-tubes and two bottles of the gas. Cover the test-tubes with paper and the bottles with glass plates.

Investigate its solubility by placing a test-tube filled with it mouth down in water. Remove the test-tube from the pan by slipping a glass plate under it, and add a few drops of litmus solution to the liquid in the tube. The reddening of the litmus shows the presence of *sulphurous acid.* How has it been formed?

Place a few drops of litmus solution in a test-tube filled with the gas, cork the tube, shake it, and let stand. What is the first action of the gas on the litmus? Why? What is the final action? Sulphur dioxide is much used for bleaching.

Lower a lighted candle into a bottle of the gas. (?) Place some *lead dioxide* in a clean deflagrating spoon and warm it gently. Lower it into a bottle of sulphur dioxide. The product is *lead sulphate*—

$$PbO_2 + SO_2 = PbSO_4$$
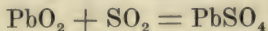
Examine it, and compare it with lead dioxide.

Pass sulphur dioxide from your generator through 100 c.c. of water, until you have a strong solution. Test the liquid with litmus paper (red and blue). Add a

dilute solution of sodium hydroxide to it drop by drop, stirring constantly until litmus paper is just turned blue. Then evaporate to dryness in a clean dish. The residue is *sodium sulphite,* Na_2SO_3, formed thus—

$$2NaOH + H_2SO_3 = Na_2SO_3 + 2H_2O$$
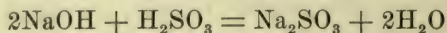
Examine it. How does it behave with hydrochloric acid? with sulphuric acid? What gas is produced when the acids act upon it? Take some sodium sulphite from the bottle and see if it behaves in the same way with acids.

Most sulphites are insoluble in water. Mix water solutions of sodium sulphite and calcium chloride. The visible product is calcium sulphite, $CaSO_3$. Write the equation. Is it soluble in water? in hydrochloric acid?

If time permits, pass a slow current of sulphur dioxide from your generator through a U-shaped tube, which is embedded in a mixture of equal parts of ice and salt. Liquid sulphur dioxide collects. Pour some of it on a *little* water in a porcelain dish. *Use the hood.* The water will be frozen by the rapid evaporation of the sulphur dioxide.

EXPERIMENT 112.—**Sulphuric acid.**—Examine sulphuric acid. How does it compare with water as regards density and consistency? Slowly pour sulphuric acid in a thin stream, stirring constantly into 5 c.c. of water in a beaker until you have added an equal volume of the acid. *Care. Never add water to sulphuric acid. Always add the acid slowly to the water, stirring constantly.* Notice the production of heat. Make some dilute sulphuric acid, and write a word with it on a sheet of paper, using a glass rod as a pen. Heat the paper over the flame, taking care not to set fire to it. Place a splinter or a match-stick in a little strong sulphuric acid in a test-tube.

Make a *little* strong hot solution of sugar and place not more than 3 c.c. of it in a test-tube. Slowly add strong sulphuric acid until a decided result is obtained.

Wood and paper are chiefly composed of a substance called cellulose, whose formula is $C_6H_{10}O_5$. The formula of sugar is $C_{12}H_{22}O_{11}$. Bearing in mind the strong attraction of sulphuric acid for water, explain the three results just obtained.

Repeat the reaction of barium chloride with sulphuric acid. (Experiment 81.)

Look through your notes from the beginning for all cases in which sulphuric acid has been used, and make a table in your notes containing the equations for the various reactions in which you have employed it. Arrange the table thus:

Reactions of Sulphuric Acid with Various Substances

Zinc....................	$Zn + H_2SO_4 = ZnSO_4 + H_2$
Sodium nitrate..........	$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$

QUESTIONS

1. What is the most recent process for the production of sulphuric acid ?

2. What is the lead-chamber process for the production of sulphuric acid ?

PROBLEMS

130. How much sulphuric acid can be made from 4 tons of sulphur ?

131. How much sulphuric acid can be made from 40 tons of pyrite, FeS_2 ?

132. The density of sulphuric acid is 1.84. How much sulphur is there in 100 c.c. of it ?

133. How many tons of sulphuric acid can be made from 100 tons of pyrite containing 48 per cent of sulphur ?

134. 1.8752 grams of cobalt, when converted into cobalt sulphate, yielded 4.9472 grams. What is the atomic weight of cobalt? Assume $S = 32$, $O = 16$. The formula of cobalt sulphate is $CoSO_4$.

CHAPTER XXXVI

No experiments.

CHAPTER XXXVII

FLUORINE

EXPERIMENT 113.—**Hydrofluoric acid.**—Mix in a lead dish—*under the hood*—some powdered calcium fluoride with about an equal weight of strong sulphuric acid. Support the dish in a ring or on a pipe-stem triangle, and apply a gentle heat. The flame should not touch the dish. *Do not inhale the gas given off. It is poisonous.* Hold over the dish a piece of red and a piece of blue litmus paper. (?) Wet a glass rod with ammonia. Be careful not to let any ammonia fall into the dish, since this would cause an explosion. Remembering the behavior of ammonia with HCl, explain its behavior with HF. Cover the dish with a clean plate of window-glass, and let it stand some hours, if possible. Remove the glass, wash it with water, and examine. Clean the dish by scraping the contents into a jar with an old knife or file.

Warm a glass plate by placing it on a ring of your stand and moving about a small flame at least 5 cm. below the plate. If the flame is brought nearer the plate it will crack it. Place some paraffin on the warm plate, and allow the melted paraffin to cover it completely. Let the plate cool and scratch a word or some lines through the wax with a pin or a knife-blade. Take the plate to

the hood, cover the word with a piece of filter paper, and carefully wet the paper with hydrofluoric acid. *Be careful. Hydrofluoric acid produces poisoned wounds on the skin, and its vapor is poisonous.* Place a paper containing a plainly written caution by the side of the plate, so that no one may touch it and be injured, and let it stand under the hood for as long a time as possible. Then take away the paper *with forceps,* and throw it into the waste jar. Take the plate with forceps and place it in a pan of boiling water. This will remove both the hydrofluoric acid and the wax. Wipe it with a towel and examine. Write the equations between calcium fluoride and sulphuric acid and between silica and hydrofluoric acid.

PROBLEMS

135. How much calcium fluoride and how much sulphuric acid containing 96 per cent H_2SO_4 are needed to make 12 grams of pure hydrofluoric acid ?

136. How much calcium sulphate and how much hydrofluoric acid are formed when 50 grams of calcium fluoride are heated with sulphuric acid ?

CHAPTER XXXVIII

BROMINE AND IODINE

EXPERIMENT 114.—**Bromine.**—*Use the hood in working with bromine. The vapor is extremely irritating. The liquid must not be gotten upon the flesh or clothing.* Powder 1 gram of potassium bromide and mix it with 2 grams of powdered manganese dioxide. Place the mixture in a wide test-tube, and fill the tube one-quarter with cold dilute sulphuric acid, 1 volume acid to 4 volumes water. Clamp the tube in an inclined position, connect it with a *well-fitting* cork and delivery tube, dipping into

an empty test-tube surrounded by cold water. Heat gently. The product is *bromine*. Examine it. The equation is similar to that given for *iodine,* on p. 258, Part I. Write it.

Examine bromine, attending especially to color, density, and volatility. Place three dry test-tubes in a rack *under the hood.* Put a little bromine in each (1 cm. deep). Notice the color of the vapor. Into one test-tube drop a piece of tin, into another a piece of antimony. Use pieces a little larger than the head of a pin, and be careful. Is bromine an energetic element. Nearly fill the third test-tube with water and cork it tightly. Shake it. Notice the color of the product, which is called *bromine-water.* Does bromine-water bleach? Try it on a little water faintly colored with litmus.

Dissolve a little potassium bromide in water in a wide test-tube. Add a layer of chloroform 2 cm. deep, cork the tube, and shake it. Do bromine *ions* give any color to water or chloroform? Now add *chlorine-water* to the liquid until the tube is nearly full, cork it, and shake it for five minutes. The color of the chloroform is due to dissolved bromine, Br_2, not bromine ions. Write the equation, first in the ordinary way; second, using the idea of ions. The chloroform and the water take no part in the chemical change, and must not appear in the equation.

Pour away the water as far as possible without losing any of the chloroform, fill up the tube with water, shake and pour off again to get rid of all chlorine. A solution of Br_2 in chloroform remains in the tube. Add more water and a crystal of potassium iodide, KI, and shake again. Notice the change in the color of the chloroform. It now contains, instead of Br_2, I_2 dissolved. Write the equation, both from the ordinary standpoint and from the standpoint of ions.

Discuss this experiment at length in your notes, and

show from it that the tendency of these three elements to exist as ions decreases in the order Cl, Br, I. Where would F come in this series?

EXPERIMENT 115.—**Hydrobromic acid.**—Place a few crystals of potassium bromide in a wide test-tube and cover with a mixture of 3 volumes of sulphuric acid and 1 volume of water. Clamp the tube in an inclined position, insert a cork with a delivery tube, and collect the gas by downward displacement in *dry* wide test-tubes. Use a gentle heat. Try the solubility in water. Try the action upon red and blue litmus paper. Let fall a drop of ammonia into a tube of the gas. Make a comparison between HBr and HCl.

EXPERIMENT 116.—**Iodine.**—Place in a mortar 1 gram of potassium iodide and 2 grams of manganese dioxide. Grind thoroughly and transfer the mixture to a porcelain dish. Add enough of a cold mixture of 1 volume strong sulphuric acid and 2 volumes water to cover the powder. Cover the dish with a funnel and apply a *gentle* heat. When the funnel is well coated with iodine-crystals, stop the experiment and scrape off the crystals. Use them for the following experiments, or, if the quantity is insufficient, obtain a little iodine from the bottle.

Examine iodine with respect to color, luster, odor, and density. Warm a dry wide test-tube *gently,* and drop a crystal of iodine into it. Invert the tube. What are the properties of iodine vapor? What about its density? If the formula of iodine is I_2, what must be the density of its vapor referred to hydrogen? referred to air?

Use the same test-tube to test the solubility of iodine in water. (?) Use the tip of a knife-blade filled with powdered iodine—not more. Add two crystals of potassium iodide and shake. (?) Preserve the solution.

Grind about 0.5 gram of starch with a little water in a mortar. Slowly pour the liquid into 100 c.c. of boiling

water in a clean dish. The liquid must be colorless. It remains colorless when a few drops of it are mixed with a little potassium-iodide solution in a test-tube. Try it. Now half fill a wide test-tube with water, add a little of your starch solution, and a drop of your solution of iodine. Notice the color, which can be used as a test both for iodine and starch. The color disappears when the tube is heated, but reappears on cooling. Try this.

Place about 3 c.c. of chloroform in a test-tube, half fill the test-tube with water, and add a drop or two of your solution of iodine in potassium iodide. Shake the tube. The color of the chloroform solution can be used as a test for iodine.

Carefully examine potassium iodide. What are the corresponding bromine and chlorine compounds? Does it resemble them? Add a few drops of potassium iodide solution to a little solution of silver nitrate. The visible product is *silver iodide,* AgI. Write the equation. Make some *silver bromide* in the same way. Do they resemble silver chloride? If you can not recall the properties of silver chloride, make a little by mixing solutions of silver nitrate and sodium chloride. Use half of each product to study the solubility of the three substances in ammonia. Stand the other half in direct sunlight, or the brightest light accessible. Record and discuss the results.

Problems

137. How much potassium bromide is required to make 50 grams of bromine?

138. 1.8 grams of potassium bromide are heated with dilute sulphuric acid. What volume of hydrobromic-acid gas at 26° is liberated?

139. What volume of hydrobromic-acid gas can be made from 160 c.c. of liquid bromine according to the method described on p. 257, Part I? Assume that bromine is 3 times as dense as water.

140. Manganese dioxide is heated with hydrochloric acid, and the chlorine passed in a solution of potassium iodide. How much iodine will be set free by the chlorine evolved when 12 grams of manganese dioxide are used?

141. Under the same circumstances as in Problem 138, how much manganese dioxide is needed to liberate 63.5 grams of iodine?

142. Under the same conditions as in the two preceding problems, how much iodine will be set free when 43.5 grams of manganese dioxide are used?

CHAPTER XXXIX

IRON

EXPERIMENT 117.—**Reduction of ferric oxide by hydrogen.**—Place a little ferric oxide in a bulb-tube and pass hydrogen, dried by passing through a U-tube filled with lumps of calcium chloride, over it. It is best to use a Kipp generator. If you employ an ordinary gas-bottle, it is necessary to wait until all air is expelled, and to wrap the gas-bottle and cork in a towel before applying heat to the bulb. Heat the bulb, gently at first. What are the two products? Let the bulb cool completely, shake out the solid material on a paper, and examine it. Is it attracted by the magnet? Is it combustible?

EXPERIMENT 118.—**Spontaneous oxidation of finely divided iron.**—Heat in a sealed tube of hard glass some *ferrous oxalate* to redness, keeping the finger loosely over the open end of the tube to prevent the entrance of air. Cork the tube tightly, let it cool, and shake out the black iron-powder into a plate or a dry dish. (?) Clearly, finely divided iron oxidizes more readily than compact iron. You have noticed frequently in your work that powdering a substance makes it dissolve more rap-

idly. The reason is the same in the two cases. What is it?

Examine the most important ores of iron, hematite (Fe_2O_3), magnetite (Fe_3O_4), and limonite, which contains both ferric oxide and ferric hydroxide. Also examine pyrite (FeS_2), which is important on account of its sulphur.

EXPERIMENT 119.—**Ferric salts.**—Dissolve a little *ferric chloride,* $FeCl_3$, in 50 c.c. of water in a beaker. Use small portions to investigate the action of the following substances upon it:

1. Ammonia water, NH_4OH, precipitates ferric hydroxide, $Fe(OH)_3$. Write the equation and record the properties of the substance.

2. *Potassium thiocyanate,* KCNS (often called potassium sulphocyanide). Dissolve a little in water for the test. Notice that a red *coloration* of ferric thiocyanate, $Fe(CNS)_3$, is obtained, not a precipitate.

3. *Potassium ferricyanide* (not *ferrocyanide*). The solution of this substance must be made up fresh and, before dissolving, the outer portion of the crystal used should be removed by running water over it. Notice that there is no *precipitate,* but a dark coloration.

EXPERIMENT 120.—**Ferrous salts.**—Examine some iron wire, and if the wire contains any rust, remove it by scraping with sandpaper. Place about 0.5 gram of the wire in a small flask, add 100 c.c. water and 15 c.c. hydrochloric acid, and close the flask with a cork bearing a valve made as shown in Fig. 25. A glass tube

FIG. 25.

fits tightly in the cork, and is connected with a piece of rubber tubing 4 cm. long, the end of which is closed by a bit of glass rod. In the middle of the rubber tube is a longitudinal slit 1 cm. long, made with the point

of a sharp knife-blade. This arrangement permits the escape of the hydrogen from the flask, but obstructs the entrance of air, which would convert the *ferrous* chloride into *ferric* compounds.

When the iron is dissolved, cool the solution of ferrous chloride by running water over the flask, and investigate the behavior of small portions with the same three substances employed in the preceding experiment. Keep the flask corked.

Notice that *ferrous* hydroxide, obtained by the action of ammonia, is at first white, but rapidly turns green, and finally becomes rust-colored *ferric* hydroxide. This change is due to absorption of oxygen from the air.

Potassium thiocyanate should produce no color. If a faint pink is produced, suggest a reason for it.

Potassium ferricyanide produces a deep blue *precipitate,* quite different in character from the result of its action upon the ferric solution.

Now take a little of your ferrous solution and add bromine-water, drop by drop, until the liquid is slightly reddish. Boil the liquid. Notice the color change. Does the new color resemble that of ferric chloride—the color of the ferric ion? Test it with the same three substances, using separate small portions, and see whether it is now *ferrous* or *ferric*. Write the equation for the action of chlorine on ferrous chloride.

Place a little of your ferrous chloride solution in a test-tube, add a few drops of nitric acid, and boil. Does it seem to change to ferric chloride? Apply the three tests and ascertain.

Place a little of your ferrous chloride solution in a beaker on wire gauze, and heat it gently for 15 minutes, allowing free air access. Test it for ferric compounds with potassium-thiocyanate solution. What is the action of air on ferrous salts?

EXPERIMENT 121.—**Reduction of ferric to ferrous solutions by nascent hydrogen.**—Dissolve not more than 0.1 gram of ferric chloride in 100 c.c. of water. Carefully clean the flask in which you dissolved the iron, place the ferric chloride solution in it, incline the flask, and slide in 3 grams of granulated zinc or cuttings of sheet zinc, add 10 c.c. of hydrochloric acid, insert the valve, place the flask on a piece of asbestos board, and apply a *gentle* heat. The flask should be heated at least ten minutes after the liquid has become colorless. Determine whether the solution is ferrous or ferric by the same three tests. What is the action of nascent hydrogen on ferric solutions? Write the equation. Hydrogen passed into a ferric solution through a glass tube has no effect. What is the theoretical explanation of this fact?

PROBLEMS

143. What volume of hydrogen at 13° and 780 mm. is needed to convert 31.5 grams of Fe_2O_3 into iron ?

144. What volume of hydrogen at 14° and 740 mm. is required to change 20 grams of ferric oxide into iron ?

145. If ferric oxide, Fe_2O_3, contains 70 per cent iron and 30 per cent oxygen, what is the atomic weight of iron ?

146. If ferrous oxide, FeO, contains 77.8 per cent iron and 22.8 per cent oxygen, what is the atomic weight of iron ?

CHAPTER XL

EXPERIMENT 122.—**Platinum.**—Dip some asbestos fiber into a solution of *platinic chloride,* $PtCl_4$. *Use the solution sparingly, and return any unused portion to the bottle. It is expensive.* Heat the asbestos to redness for a few seconds, holding it in forceps. The result of this operation is to coat the asbestos with finely divided plat-

inum. What gas must have escaped? What is the effect of heat upon compounds of platinum?

Let the " platinized asbestos," as it is called, cool, hold it in forceps, and allow hydrogen from a jet connected with a Kipp generator to stream out against it. The generator must be free from air, or an explosion will result. If there is any doubt about this, let hydrogen escape from it at the rate of a bubble a second, dipping the exit-tube in water for ten minutes before the experiment is tried. Describe and explain the result.

CHAPTER XLI

CARBON

EXPERIMENT 123.—**Allotropic forms of carbon.**—Examine graphite, charcoal, anthracite and bituminous coal. Describe them. Describe the diamond. Make some lampblack by holding a piece of chalk in a luminous gas flame and examine and describe it.

Color some water faintly with litmus. The liquid must be clear and free from any solid matter. Filter it, if necessary, and add to it 3–5 grams of *animal charcoal* (bone-black). Warm the liquid gently, shake for a time, and filter. If the liquid is not colorless, filter it again. Repeat, using water colored with a *little* ink (one drop) or indigo, instead of the litmus. This remarkable property of decolorizing liquids is also possessed by wood charcoal, but to a far less degree.

EXPERIMENT 124.—**Illuminating gas.**—Fill a hard glass test-tube one-quarter with bituminous coal, clamp it horizontally near the cork, and apply a heat, at first gentle and finally intense. During the heating disconnect sev-

eral times and test the gas in the hard glass tube for ammonia with red litmus paper. Notice the production of tar during the heating. Collect the gas given off over water in wide test-tubes. Examine it, especially with regard to combustibility. Examine the residue left in the tube, which is *coke*.

CHAPTER XLII

CARBON DIOXIDE AND CARBON MONOXIDE

You have already made experiments which prove that carbon dioxide is produced by the burning of charcoal in the air or in oxygen, and that it is contained in the atmosphere and in the gases from the lungs. Read again your notes of these experiments, and if you have forgotten any essential point, repeat them.

EXPERIMENT 125.—**Production of carbon dioxide by combustion.**—Fill a deflagrating spoon with powdered charcoal, heat it to redness, and let it burn in a covered bottle. Test the gas with lime-water.

Hold a dry clean bottle over a *small* gas flame for a few seconds and apply the lime-water test. Repeat with a candle flame. With burning wood (match-stick). With the flame of kerosene. Of alcohol. (The last two flames can be conveniently obtained by dipping a bunch of asbestos into the corresponding liquid, placing it on an iron plate and setting fire to it.

Draw conclusions regarding the existence of carbon in combustibles and the products of their combustion. State the evidence.

EXPERIMENT 126.—**Production of carbon dioxide by the action of acids on carbonates.**—Place a little sodium

carbonate in each of three small beakers, and set each in a larger beaker or in a bottle or cylinder. Add to the first hydrochloric acid, to the second nitric, and to the third sulphuric. Cover the larger vessels with paper. When the action is over, remove the small beakers with forceps, add lime-water to each of the larger vessels, and shake. What does this experiment prove? Write the three equations.

EXPERIMENT 127.—**Preparation of carbon dioxide.**— Use the apparatus employed in making hydrogen. Place the gas-bottle almost horizontal and slide enough broken marble into it to fill it when upright to the depth of 1 cm. If the lumps are too large they can be broken with a hammer on an anvil—not in a mortar. Add 50 c.c. of water, and then hydrochloric acid, slowly through the funnel-tube until a brisk evolution of gas is obtained. Collect it by downward displacement in dry bottles.

Investigate the physical properties of the gas. Has it any odor or taste? If in doubt about the last point, let the gas from the generator bubble through a little water in a test-tube and taste the liquid. Test its solubility in water in the usual way.

Lower a lighted candle into a bottle of the gas. In order to illustrate its high density, place a lighted candle on your desk and pour carbon dioxide over it, just as you would pour water. Balance a large beaker on the platform scales and pour a bottle of the gas into it.

A few substances, which produce very high temperatures by their combustion, will burn in the gas. Try a piece of magnesium ribbon, held in forceps and started burning in the air. What is the black substance which is obtained along with the magnesium oxide?

Pass carbon dioxide through some lime-water in a test-tube for some time. Notice that the calcium carbonate which it at first precipitated finally redissolves. Calcium

carbonate is soluble in water containing carbon dioxide, and this solution is present in many " hard waters."

Boil the liquid, and show that when the carbon dioxide is expelled the precipitate is again obtained.

EXPERIMENT 128.—**Action of glowing charcoal on carbon dioxide.**—Pass carbon dioxide from a Kipp generator over a column of glowing charcoal about 20 cm. long in a combustion-tube. The tube is heated slowly and carefully by a wing-top burner. Red rubber stoppers are best for it, but ordinary corks will answer with care. From this tube the gas passes through a solution of potassium hydroxide in a flask with a doubly perforated cork. It enters through a tube which goes almost to the bottom of the flask, and leaves through a tube which ends just inside the cork and does not dip into the liquid. This tube conveys the gas to a pan, where it is collected over water in wide test-tubes. The current of gas must be very slow.

Study the properties of the carbon monoxide, CO. Especially notice its combustion. *It is highly poisonous, and must not be inhaled.* Apply the lime-water test to the product of its combustion.

EXPERIMENT 129.—**Preparation of carbon monoxide by heating oxalic acid with sulphuric acid.**—Place 8–10 grams of oxalic acid and 50–70 grams of strong sulphuric acid in a small flask. Fit the flask with a doubly perforated cork, one hole of which carries a safety-funnel. A little mercury must be placed in the bend of the safety-funnel. Apply a very gentle heat. The gas is led through a wash-bottle containing potassium hydroxide and collected over water. The first two bottles of gas contain air, and should be allowed to escape under the hood. Investigate the properties of the gas, study its combustion by burning a bottle full of it, and test the product of the burning by lime-water.

Care must be taken not to inhale the gas produced in this experiment. In heating the flask, use a small flame, which should be removed or turned down if the contents begin to froth up. Keep the hand away from under the flask in heating, for it may break, and hot sulphuric acid attacks the flesh energetically.

QUESTIONS

1. Why is carbon monoxide poisonous?

2. Why is it no longer poisonous when the air pressure is greatly increased?

3. What volume of carbon dioxide will be produced by the burning of a liter of carbon monoxide? Why? What volume of oxygen is needed?

PROBLEMS

147. The great German chemical works, the Badische Anilin-und Soda Fabrik, burns 190,000 tons of coal a year. If the coal contains 70 per cent of carbon, and if there are 310 working days in the year, what weight of CO_2 escapes daily from the chimneys of the establishment?

148. What volume of carbon dioxide is formed by the burning of 30 liters of carbon monoxide, and what volume of oxygen is required? Solve by inspection.

149. What gas gives rise to the blue flame often seen playing over the surface of a coal fire? How much coal containing 90 per cent of carbon would be needed to make 5,000 liters of this gas at 15° and 750 mm.?

150. What volume of gas measured under standard conditions is produced when 20 grams of pure dry oxalic acid are heated with strong sulphuric acid? What is the composition of the gas?

151. What volume of carbon dioxide must be passed over glowing charcoal to form 42 grams of carbon monoxide?

152. What is the volume (*a*) of 50 grams of carbon monoxide? (*b*) Of 50 grams of carbon dioxide?

153. What volume of carbon dioxide would be produced by burning a diamond weighing 3 grams in oxygen?

154. How much carbon is there in (*a*) 2.8 liters of carbon dioxide? (*b*) 2.8 liters of carbon monoxide?

155. What volume of carbon dioxide at standard conditions is produced by dissolving 25 grams of marble in hydrochloric acid ?

156. What volume of carbon dioxide at 12° and 750 mm. is produced by dissolving 20 grams of marble in hydrochloric acid ?

CHAPTER XLIII

SOME CARBON COMPOUNDS

EXPERIMENT 130.—**Methane.**—Heat some *sodium acetate* in an iron dish until the water of crystallization has escaped and the melted dry salt is left. Mix 3 grams of this in a mortar with 3 grams of lime and 3 grams of sodium hydroxide. Grind thoroughly and transfer the mixture to a hard glass test-tube. Clamp the tube horizontal and fit it with a cork bearing a delivery tube. Apply a gentle heat, gradually increased to redness. Collect the gas in wide test-tubes. Cover the hard glass test-tube with soot, and disconnect before letting it cool.

Record the physical properties of the gas. Burn some, notice the character of the combustion, and apply the lime-water test.

EXPERIMENT 131.—**Acetylene.**—Fill a small test-tube one-third with water and throw a piece of *calcium carbide* into it. Has the gas any color or odor? Light it. Does its combustion resemble that of methane? Record the physical properties of calcium carbide.

EXPERIMENT 132.—**Various carbon compounds.**—*Ether, wood alcohol, and carbon disulphide are highly inflammable, and must not be used when a flame is anywhere in the neighborhood. The bottles containing them must be kept tightly corked.*

Examine the following important carbon compounds and record their properties. Study also their solubility

in water. *Alcohol, ether, chloroform, wood alcohol* (methyl alcohol), and *carbon disulphide.* Briefly state in your notes the source and uses of each.

EXPERIMENT 133. — **Fermentation.** — Dissolve 100 grams of grape-sugar (glucose) in a liter of water. Mix half of a compressed yeast cake to a thin paste with water and add it to the liquid. Place the mixture in a flask closed by a singly perforated cork bearing a tube which leads to a small flask containing 50 c.c. of lime-water. The tube should dip into the lime-water. This flask is closed by a doubly perforated cork, and a tube from the second hole is connected with a U-tube containing pieces of sodium hydroxide. This is to prevent the CO_2 of the air from entering the flask containing the lime-water.

Let the apparatus stand several days, if possible. What change occurs in the lime-water? What gas must have been given off? What is the other product?

To obtain it, distill the liquid in the large flask in the apparatus employed for the distillation of water (Fig. 5). Continue distilling until $\frac{1}{10}$ of the liquid has passed over, and discard the rest. If there is too much liquid to be distilled in one operation, divide it into several portions, and distill $\frac{1}{10}$ of each. The flask should not be more than $\frac{2}{3}$ filled. Unite these distillates in a small flask, and distill $\frac{1}{10}$ of the liquid, using a dry test-tube as a receiver. Has the liquid which distills the odor of alcohol? Is it combustible? If not, place some in a dish, heat it, and hold a lighted match near the surface of the liquid.[1]

EXPERIMENT 134.—**Aldehyde.**—Make a strong solution of *potassium dichromate,* place it in a test-tube, and add 1 c.c. of strong sulphuric acid and 1 c.c. of alcohol. Heat the liquid. The odor produced is that of *aldehyde.* Notice the change from the red color of potassium di-

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[1] This distillation consumes much time and is not always successful. It is sufficient to notice the production of CO_2 and the general nature of the process.

chromate to the green color of *chromium sulphate,*
$Cr_2(SO_4)_3$.

EXPERIMENT 135.—**Acetic acid.**—Examine acetic acid
and record its properties. Dilute some with 100 times its
volume of water, and test the liquid with litmus paper
(red and blue). Taste it. Mix 5 c.c. of strong acetic
acid with 10 c.c. of alcohol. If possible, preserve some of
the liquid in a corked test-tube, and notice the gradual
development of the fragrant odor of *acetic ether.* This
is an interesting example of slow chemical change. Sul-
phuric acid catalytically accelerates the process. Add to
some of the fresh mixture in a test-tube 2 c.c. of strong
sulphuric acid and heat gently. The odor appears at once.
This is a *test* for acetic acid or for alcohol.

Examine *vinegar,* taste it, and try its behavior with
red and blue litmus paper.

Examine *sodium acetate,* and notice its similarity in
general character to ordinary sodium salts, like the nitrate
and the sulphate.

QUESTIONS

1. What is fire-damp, and how is it formed ?

2. What is the valence of carbon in CH_4, C_2H_6, C_3H_8, $CHCl_3$,
C_2H_5Cl ?

3. What is a *substitution product?* Give examples. Why are
substitution products so numerous ?

4. Write the formulas of the first nine of the series of hydro-
carbons which begins with *methane.* How do the physical proper-
ties of the substances change as we advance in the series ?

5. Why is it that a mixture of methane or any other combusti-
ble gas with air will *explode,* although the gas alone will burn
quietly ?

6. What is fermentation ? State briefly two methods by
which it has been proved that fermentation is not caused by any
vital activity of yeast.

PROBLEMS

157. What is the weight of 38 liters of methane at 31°?

158. What is the weight of 10 liters of acetylene?

159. How much calcium carbide is needed to produce 5.6 liters of acetylene?

160. A town is to be lighted with acetylene. It is calculated that the consumption of the gas will be 70,000 liters per day. How much calcium carbide will be required per month of thirty days?

161. How much carbon is there in 32 liters of acetylene?

162. How much sodium acetate is needed to make 8 liters of methane?

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$
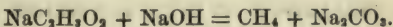
163. How many liters of oxygen at 10° and 780 mm. are needed to burn completely the methane obtained when 41 grams of sodium acetate are heated with sodium hydroxide?

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$
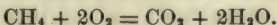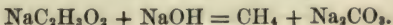
164. Calcium carbide is treated with water and the acetylene burned. 28 liters of carbon dioxide at 15° and 740 mm. resulted from the combustion. How much calcium carbide was taken, and what volume of oxygen at 15° and 740 mm. was needed to burn the acetylene?

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$
$$C_2H_2 + 5O = 2CO_2 + H_2O.$$
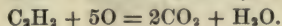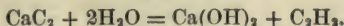
CHAPTER XLIV

ADDITIONAL CARBON COMPOUNDS

EXPERIMENT 136.—Soap.—Dissolve 25 grams of sodium hydroxide in 150 c.c. of water in an iron dish. Add 75 grams of *lard,* and boil gently for half an hour or more. Slowly add 50 grams of salt, stirring constantly. *Be careful during the boiling not to allow any of the*

*liquid to be spattered into the eyes. It is well to keep
a glass plate between the dish and the face.*

The solid which separates at the top is *soap*. What
else has been produced, and where is it? Remove the
soap and examine it. It is a mixture of the sodium salts
of *palmitic, stearic,* and *oleic acids.* Dissolve about 3
grams of shavings of it in 100 c.c. of warm water in a
dish. Add dilute sulphuric acid to a portion of it. The
mass which separates consists of a mixture of the acids
mentioned above, which are liberated from their sodium
salts by the sulphuric acid, sodium sulphate being formed.
To another small portion of the soap solution add a dilute
solution of *calcium chloride.* Water containing calcium
compounds is said to be *hard.* Why can not hard water
be used satisfactorily in washing with soap?

EXPERIMENT 137.—**Albumin.**—Break an egg and sepa-
rate some of the white from the yolk. Dilute about 5 c.c.
of the white of egg with 100 c.c. of water. Boil a portion
of this liquid in a test-tube. (?) To another portion in
a test-tube add a little nitric acid. The albumin is pre-
cipitated in both experiments.

Heat a bit of meat, a feather, a few clippings of horn,
or a cochineal insect in a dry test-tube. Almost any form
of animal matter will answer. Describe the nature of the
change. Notice the odor. Show by red litmus paper that
ammonia is given off. This proves that nitrogen and hy-
drogen are two of the constituents of albumin. Look for
evidence of the presence of carbon in the residue in the
tube.

CHAPTER XLV

No experiments.

CHAPTER XLVI

No experiments.

Additional exercise. The fundamental principles of qualitative analysis.[1]—A. Prepare dilute solutions of the nitrates of *silver, copper, iron, barium,* and *sodium.* About 100 c.c. of each will be needed. Copper nitrate can be made by heating a little copper in a test-tube with *dilute* nitric acid until the action ceases. The liquid should still contain undissolved copper. It is diluted and filtered if necessary, or simply poured off from the copper. Iron nitrate (ferric) can be made in a similar way, but the iron must be well covered with water and the nitric acid added drop by drop, for the action is violent. The other solutions can be made by dissolving 1 gram of the corresponding nitrate in 100 c.c. of water.

Study the behavior of small portions of each of these liquids with the following substances separately:

B. Hydrochloric acid, sulphuric acid, hydrogen sulphide, ammonium hydroxide.

The experiments should be made in test-tubes. The liquids in B should be added one drop at a time, stirring constantly. Note especially whether a precipitate or a color is produced, and if the former, whether it is soluble in excess. The hydrogen sulphide can be taken from a Kipp generator. Use a *gentle* current of the gas, not more than a bubble every two seconds. *The tube through which the H_2S passes into the liquid must be cleaned*

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[1] The object of this exercise is not to teach qualitative analysis, but to give the student a grasp of the principles upon which the separation of one metal from another depends, so that he will be able afterward to attack the subject understandingly. The scheme is that of Professor Richards (Harvard Requirements, p. 20).

both from liquid and solid before using it again for a fresh test, and every test-tube and beaker employed must be absolutely clean. If no Kipp generator is available, make the hydrogen sulphide yourself by the method already studied. *Be careful not to inhale it unnecessarily.*

NOTE.—The precipitate formed when the solution of ferric nitrate is treated with H_2S contains no iron. It is sulphur. The change in the color of the liquid will show you that the iron is now in the *ferrous* condition.

QUESTIONS

1. Devise a method of separating *silver* from any of the metals in A based on the use of hydrochloric acid. Try it, mixing a little of the silver-nitrate and copper-nitrate solutions for the purpose. Why is it necessary to wash the precipitate by filling the filter with water and letting it drain off half a dozen times after filtering? This must *always* be done in work of this kind. In the present exercise the wash liquid can be thrown away. Of course, if the work is *quantitative* it must be retained. Why is it necessary to add the hydrochloric acid until it produces no further precipitate? This is *always* necessary in similar cases. How can you prove that the precipitate is really silver chloride? How could you tell after filtering whether the silver had all been precipitated or not?

2. Devise a method of separating *barium* from any of the others. Try it with barium and copper nitrates.

3. Devise and carry out a method of separating silver, copper, and barium, when all three are present together.

4. Devise and carry out a method of separating copper from sodium by hydrogen sulphide. Evaporate the liquid, which should contain the sodium, to dryness, and apply the flame test. Identify the copper as in 5 *b* (next paragraph).

5. Separate copper from iron by hydrogen sulphide. (*a*) Heat the filtrate containing the *ferrous* ions to gentle boiling for twenty minutes to drive off the H_2S. Add a few drops of nitric acid, and boil. What change occurs in the condition of the iron? Show that the liquid contains iron, using ammonium hydroxide. (*b*) Dissolve the copper sulphide by repeatedly pouring the same portion of hot dilute nitric acid through the filter. The blue liquid

contains *copper nitrate*. Refer to your previous notes for several methods of identifying copper in it, and apply them.

6. Separate iron from sodium, using ammonium hydroxide.

7. Devise and carry out a method of separating copper, iron, and sodium when all three are present together.

8. Devise and carry out a method for the separation of all five of the metals in A, using only the substances in B for the separation. Any method you are familiar with can be used to identify the metals when separated,

APPENDIX

CALCULATION OF THE EFFECT OF TEMPERATURE, PRESSURE, AND WATER-VAPOR ON THE VOLUMES OF GASES

1. **Temperature.**—The *absolute temperature* is the temperature measured from 273° below 0° C. Thus, the absolute temperature of 10° is $273 + 10 = 283°$.

The absolute temperature of —10° is $273–10 = 263°$.

PROBLEM

165. Calculate the absolute temperature corresponding to the following centigrade temperatures :

    a. 13°.   *b.* 274°.   *c.* — 50°.   *d.* — 273°.

The volume of a mass of gas is directly proportional to its absolute temperature. Let T and $t =$ two temperatures—both absolute. Let V_T be the volume at $T°$ and V be the volume at $t°$. Then—

$$V_T = V_t \times \frac{T}{t}.$$

In words, this means if you know the volume of a mass of gas at some known temperature, you can calculate its volume at some other temperature by multiplying the old volume by the new temperature, and dividing by the old temperature, both temperatures being absolute.

Never make the error of using ordinary centigrade temperatures instead of absolute temperatures. It is easy to see that this leads directly to absurd results. For in-

stance: I have a liter of gas at 0° C. What will its volume become at 273° C.?

Here, if we use ordinary centigrade degrees, the volume becomes

$$1 \times \frac{273}{0};$$

that is, the volume is infinite—which is absurd. But if we employ absolute degrees, the volume is—

$$1 \times \frac{546}{273} = 2 \text{ liters};$$

which is the correct result.

PROBLEMS

166. What volume will a liter of air at 0° C. occupy at 100° C. ?

167. 5 liters of oxygen at 0° C. occupy what volume (*a*) at 10° C. ? (*b*) at —10° C. ?

168. 25 c.c. of nitrogen at 15° C. will measure what at the standard temperature 0° C. ?

169. I have 500 c.c. of hydrogen at 13° C. What will the volume become at 65° C. ?

170. 600 c.c. of oxygen at 28° C. will measure what at —14° C. ?

171. 500 liters of air at 20° C. will occupy what volume at 80° C.?

172. A liter of steam at 100° C. will occupy what volume at 120° C.?

173. 67 liters of air are heated from —30° C. to 60° C. ? What is the new volume ?

Since the volume of a mass of gas varies with the temperature, it is always necessary, in measuring gases, to know the temperature of the gas measured. And it is clear that the expression " 1 liter of oxygen " has no meaning unless some particular temperature is either stated or understood. Now, in order to avoid the necessity of continually stating the temperature, it is extremely convenient to assume some temperature as a standard

point which is to be understood unless some other temperature is stated. *The standard temperature universally agreed upon is 0° C.—the melting-point of ice.* Thus, when a writer speaks of "1 liter of oxygen" without stating the temperature under which the gas was measured, we know that 0° C. is meant.

The student should grasp the fact that every problem like those just solved is supposed to deal with a certain fixed weight of gas which is not added to or subtracted from during the process of heating or cooling. Clearly, if temperature and pressure remain the same, the volume must be directly proportional to the weight of the gas. Thus, 1 gram of hydrogen at standard temperature and pressure occupies a volume of 11.2 liters. Evidently, 2 grams of hydrogen must measure 22.4 liters under the same conditions, and so on. But, in all problems of this sort, the quantity of gas is supposed to remain the same.

2. **Pressure.**—*The volume of a mass of gas is inversely proportional to the pressure upon it.* If p and P are two pressure, both stated in millimeters of mercury, and if V_p and V_P are the volumes which the same quantity of gas will occupy at those pressures, then

$$V_P : V_p :: p : P. \quad \text{Hence}$$
$$V_P = V_p \times \frac{p}{P}.$$

Therefore, if the volume of a mass of gas is given at some pressure and it is required to calculate its volume at some other pressure, we must multiply the old volume by the old pressure and divide by the new pressure.

Problems

174. 10 liters of gas at a pressure of 743 mm. will occupy what volume at 720 mm. ?

175. 18.5 c.c. of nitrogen are measured under a pressure of 745 mm. What will the volume be at 760 mm. ?

176. A liter of oxygen is measured at 760 mm. What will it measure at 748 mm. ?

177. 100 c.c. of air at 760 mm. (1 atmosphere) will occupy what volume under 20 atmospheres ?

178. What pressure is required to compress 500 c.c. of carbon dioxide at 728 mm. to a volume of 400 c.c. ?

179. What must the pressure be made in order to allow the 500 c.c. of gas of the preceding problem to expand to 850 c.c. ?

In order not to be compelled to state continually the pressure, in speaking of the volumes of gases, and in order to be able to compare gas volumes, measured at different temperatures, with each other, *760 mm. of mercury is agreed upon as the standard pressure, which is understood when no pressure is stated.* This pressure is called 1 atmosphere, because the pressure of the air does not vary widely from that amount.

Since, as we have seen, 0° is the standard temperature, the expression "standard conditions" means 0° and 760 mm. Thus, when a writer speaks of 1 liter of oxygen (or of any volume of any gas) without mentioning either temperature or pressure, we understand at once that the gas is supposed to exist at 0°, and under a pressure of 760 mm.

3. *When temperature and pressure both vary,* we have simply to correct for both by the methods already studied. This can be done in two separate calculations, but it is easier and better to unite both corrections in one operation. The volume of a gas is directly proportional to the absolute temperature and inversely proportional to the pressure. Let

V_{PT} = the volume at the absolute temperature T and pressure P.

V_{pt} = the volume at the absolute temperature t and pressure p.

Then
$$V_{PT} = V_{pt} \times \frac{T}{t} \times \frac{p}{P}.$$

In words, this means that in order to calculate the new volume of a gas at some new temperature and pressure, *we must multiply the old volume by the new temperature and the old pressure, and divide it by the old temperature and the new pressure.* Of course, both temperatures must be absolute.

Such calculations can be rapidly, easily, and correctly made by the use of *logarithms,* and this is true of chemical calculations generally. A table of logarithms is given for this purpose, and its use will save about half the time and labor of chemical calculation, and will greatly reduce the number of errors in the numerical work.

PROBLEMS

180. 100 c.c. of oxygen at 15° C. and 740 mm. will occupy what volume at standard conditions?

$$V_{PT} = 100 \times \frac{273}{288} \times \frac{740}{760} = 92.3 \text{ c.c.}$$

The student will find that his chief difficulty in solving problems like this and the following ones is in determining which temperature and pressure to put in the numerator and which in the denominator. It will pay to make it a rule to inspect the fractions with great care before working out the calculation. Errors can be detected by the exercise of a little common sense. For instance, in the preceding problem the gas is to be cooled from 15° C. to 0° C. This will *reduce* its volume. Hence, the temperature-fraction must be $\frac{273}{288}$, not $\frac{288}{273}$. Also, the pressure is to be raised from 740 to 760, and this also will *reduce* the volume. Hence, the pressure fraction must be $\frac{740}{760}$, not $\frac{760}{740}$.

181. Supposing the initial temperature in the preceding problem to be −15° C. instead of 15° C., what would be the new volume? The other figures remain the same.

182. What volume will 48 c.c. of nitrogen at standard **conditions** occupy at 18° C. and 733 mm. ?

183. 25 liters of a gas at standard conditions are cooled to −10° C., and the pressure reduced to 723 mm. What is the new volume ?

184. 310 c.c. of hydrogen at 10° C. and 530 mm. will occupy what volume at 18.7° C. and 590 mm. ?

185. 1,704 c.c. of nitrogen at 11° C. and 760 mm. are brought to a temperature of 27° C. and a pressure of 900 mm. What is the volume ?

186. 271 c.c. of hydrogen at 269° C. and 900 mm. are cooled to −51° C., and the pressure decreased to 666 mm. Calculate the final volume.

4. *The effect of water-vapor on the volume of a mass of gas.*—Suppose that we have 100 c.c. of dry oxygen confined over mercury in a graduated tube. Let us admit a drop of water and allow the oxygen to saturate itself with moisture. Clearly, the volume of gas in the tube must increase, for the water-vapor will occupy space. The result is the same as though we had introduced a little nitrogen or some other gas into the tube and allowed it to mix with the oxygen.

The volume can be kept 100 c.c. by increasing the pressure under which the gas is measured. But if this is done, the total pressure can not be considered as exerted upon the oxygen in the tube, for the water-vapor is also present. Hence, the pressure under which the gas really exists and is measured is *less* than the total pressure. How much less?

The pressure which saturated water-vapor exerts at various temperatures is given in the table. When a gas is measured *over water,* or when it is measured saturated with water, *the pressure which water-vapor exerts at the temperature of measurement must be ascertained from the table and deducted from the total pressure. The remainder will be the pressure under which the gas is really measured.*

PROBLEMS

187. A mass of air at 15.3° C. and 747.2 mm., measured *over water*, occupied a volume of 82.4 c.c. What volume would it occupy dry and at standard conditions?

SOLUTION

From the table we observe that water-vapor at 15° C. exerts a pressure of 12.7 mm. and at 16° C. a pressure of 13.54 mm. Hence its pressure at 15.3° C. must = 12.9 mm.

The pressure under which the gas is really measured is

$$747.2 - 12.9 = 734.3 \text{ mm.}$$

The rest of the calculation is the same as in the preceding problems:

$$82.4 \times \frac{273}{288.3} \times \frac{734.3}{760} = 75.39 \text{ c.c.}$$

188. 11.41 c.c. of a mixture of oxygen and hydrogen are measured over water at 14° C. and 743 mm. Calculate the volume under standard conditions.

189. 112.1 c.c. of nitrogen saturated with water at 16° C. and 744 mm. will occupy what volume dry and under standard conditions?

190. The gas-holder of a gas-works contains 4,500 cubic meters of illuminating gas, confined over water. The temperature is 9° C. and the pressure 776 mm. How many cubic meters would the gas measure under standard conditions?

191. 100 c.c. of oxygen are confined over water and measured at 14° C. and 756 mm. What will be the volume when the gas is dried and placed under standard conditions?

192. A gas-holder contains 10 liters of air confined over water at 20° C. and 756 mm. What will the gas measure when dried, other conditions remaining the same?

TABLE OF ATOMIC WEIGHTS

NAME.	Symbols.	Exact values.	Approximate values.	NAME.	Symbols.	Exact values.	Approximate values.
Aluminium	Al	27.1	27	Neodymium	Nd	143.6	......
Antimony	Sb	120.0	120	Neon..............	Ne	19.94	.....
Argon..............	A	39.92	......	Nickel............	Ni	58.70	58.7
Arsenic	As	75.0	75	Nitrogen	N	14.04	14
Barium............	Ba	137.43	137	Osmium	Os	190.8	......
Beryllium.........	Be	9.1	......	Oxygen..........	O	16.000	16
Bismuth	Bi	208.0	208	Palladium	Pd	106.5	......
Boron..............	B	11.0	11	Phosphorus...:...	P	31.0	31
Bromine..........	Br	79.955	80	Platinum..........	Pt	195.2	195
Cadmium.........	Cd	112.3	112	Potassium	K	39.14	39
Caesium	Cs	132.9	......	Praseodymium ...	Pr	140.5	......
Calcium............	Ca	40.1	40	Radium...........	Ra	225.?	......
Carbon.............	C	12.001	12	Rhodium..........	Rh	103.0	.....
Cerium	Ce	140.0	......	Rubidium.........	Rb	85.44	.....
Chlorine..........	Cl	35.455	35.5	Ruthenium........	Ru	101.7	......
Chromium.........	Cr	52.14	52	Samarium........	Sa	150.0	......
Cobalt..............	Co	59.00	59	Scandium.........	Sc	44.0	......
Columbium........	Cb	94.0	......	Selenium.........	Se	79.2	. ....
Copper	Cu	63.60	63.5	Silicon............	Si	28.4	28.5
Erbium...........	Er	166.0	......	Silver............	Ag	107.93	108
Fluorine	F	19.05	19	Sodium	Na	23.05	23
Gadolinium	Gd	156. ?	......	Strontium	Sr	87.68	87.5
Gallium...........	Ga	70.0	......	Sulphur..........	S	32.065	32
Germanium........	Ge	72.5	......	Tantalum.........	Ta	183.0	......
Gold	Au	197.3	197	Tellurium.........	Te	127.5 ?	......
Helium............	He	3.96	.....	Terbium..........	Tb	160.0	......
Hydrogen..........	H	1.0075	1	Thallium..........	Tl	204.15	. ....
Indium	In	114.0	......	Thorium..........	Th	233.0	......
Iodine.............	I	126.85	127	Thulium..........	Tu	171.0 ?	......
Iridium	Ir	193.0	.....	Tin................	Sn	119.0	119
Iron...	Fe	55.9	56	Titanium..........	Ti	48.17	......
Krypton...........	Kr	81.7	......	Tungsten..........	W	184.0	......
Lanthanum........	La	138.5	......	Uranium..........	U	238.5	239
Lead...............	Pb	206.92	207	Vanadium	V	51.4	.....
Lithium............	Li	7.03	......	Xenon	X	128.0	......
Magnesium...,....	Mg	24.36	24	Ytterbium........	Yb	173.0	......
Manganese	Mn	55.02	55	Yttrium	Y	89.0	......
Mercury	Hg	200.0	......	Zinc	Zn	65.40	65.5
Molybdenum	Mo	96.0	......	Zirconium.........	Zr	90.6	......

This table contains the values of the atomic weights according to the calculations of Prof. Richards. The *approximate* values should be used in solving all problems.

Vapor Pressure of Water

Tempera-ture, Centi-grade.	Vapor pressure in mm. of mercury.	Tempera-ture, Cen-tigrade.	Vapor pressure in mm. of mercury.	Tempera-ture, Cen tigrade.	Vapor pressure in mm. of mercury.
−10	2.09	12	10.46	26	24.99
− 5	3.11	13	11.16	27	26.51
0	4.60	14	11.91	28	28.10
+ 1	4.94	15	12.70	29	29.78
2	5.30	16	13.54	30	31.55
3	5.69	17	14.42	35	41.83
4	6.10	18	15.36	40	54.91
5	6.53	19	16.35	50	91.98
6	7.00	20	17.39	60	148.79
7	7.49	21	18.50	70	233.09
8	8.02	22	19.66	80	354.64
9	8.57	23	20.89	90	525.45
10	9.17	24	22.18	100	760.00
11	9.79	25	23.55		

The vapor pressure of water for a temperature not given in the table can easily be found by calculation. Thus, suppose it is required to find the vapor pressure for the temperature of 32.5°. The increase in vapor pressure from 30° to 35° is $41.83 - 31.55 = 10.28$ mm. Hence, the increase from 30° to 32.5° will not be far from $10.28 \times \dfrac{2.5}{5}$, or 5.14 mm., and the vapor pressure for 32.5° will be about 36.69 mm. It will not be exactly 36.69 mm., because, in the calculation, it is assumed that the vapor pressure increases proportionally with the temperature, which is not the case, but for small differences of temperature the error is small.

When a gas is measured over water, or moist, the vapor pressure of water for the temperature must be subtracted from the pressure under which the gas is measured.

Factors for converting Metric into Ordinary Units

<div align="center">

1 inch = 2.54 cm.   1 cm. = 0.3937 in.

</div>

For practical purposes it is sufficient to remember that about $2\frac{1}{2}$ cm. = 1 in.

A *liter* is the volume of a cube whose side is 10 cm. Therefore,

$$1 \text{ liter} = 1,000 \text{ cubic centimeters};$$
$$1 \text{ pint} = 0.47318 \text{ liter};$$
$$1 \text{ gallon} = 3.78543 \text{ liters};$$
$$1 \text{ liter} = 0.26417 \text{ gallon}.$$

The *gram* is the weight of 1 c.c. of pure water at 4°.
1 liter of pure water at 4° = 1 kilo (1,000 grams).

1 oz. = 28.35 gms.   1 gram = 15.432 grains.
1 lb. = 453.6 gms.   1 kilo = 2.2046 lbs.

Formulæ for converting Fahrenheit Degrees into Centigrade, and the Reverse

$$C.° = \frac{5}{9}(F.° - 32).$$

$$F.° = \frac{9}{5}C.° + 32.$$

Miscellaneous Data

Weight, 1 liter pure hydrogen at 0° and 760 mm. = .0896 gram. Volume of molecular weight in grams of any gas or vapor, 22.4 liters.

Melting-point of ice................. 0° C.
"   " alcohol............ −130° C.
"   " mercury.......... −39.4° C.
"   " hydrogen, about.... −260° C.
"   " tin............... 233° C.
"   " lead.............. 334° C.
"   " silver .... 954° C.
"   " gold .... 1,064° C.
"   " iron (pure) .... 1,600° C.

Boiling-point of water.... .... 100° C.
"   " alcohol .... 78° C.
"   " ether .... 35° C.
"   " chloroform .... 61.5° C.
"   " carbon disulphide... 47° C.
"   " hydrogen .... −252.8° C.
"   " oxygen .... −183° C.

Air contains 21 per cent (20.97 per cent) by volume of oxygen. 1 liter of dry air at 0° and 760 mm. weighs 1.293 grams.

Logarithms.

Proportional parts

Nat. Number	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	·9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

Logarithms.

Nat. Number	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
·	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
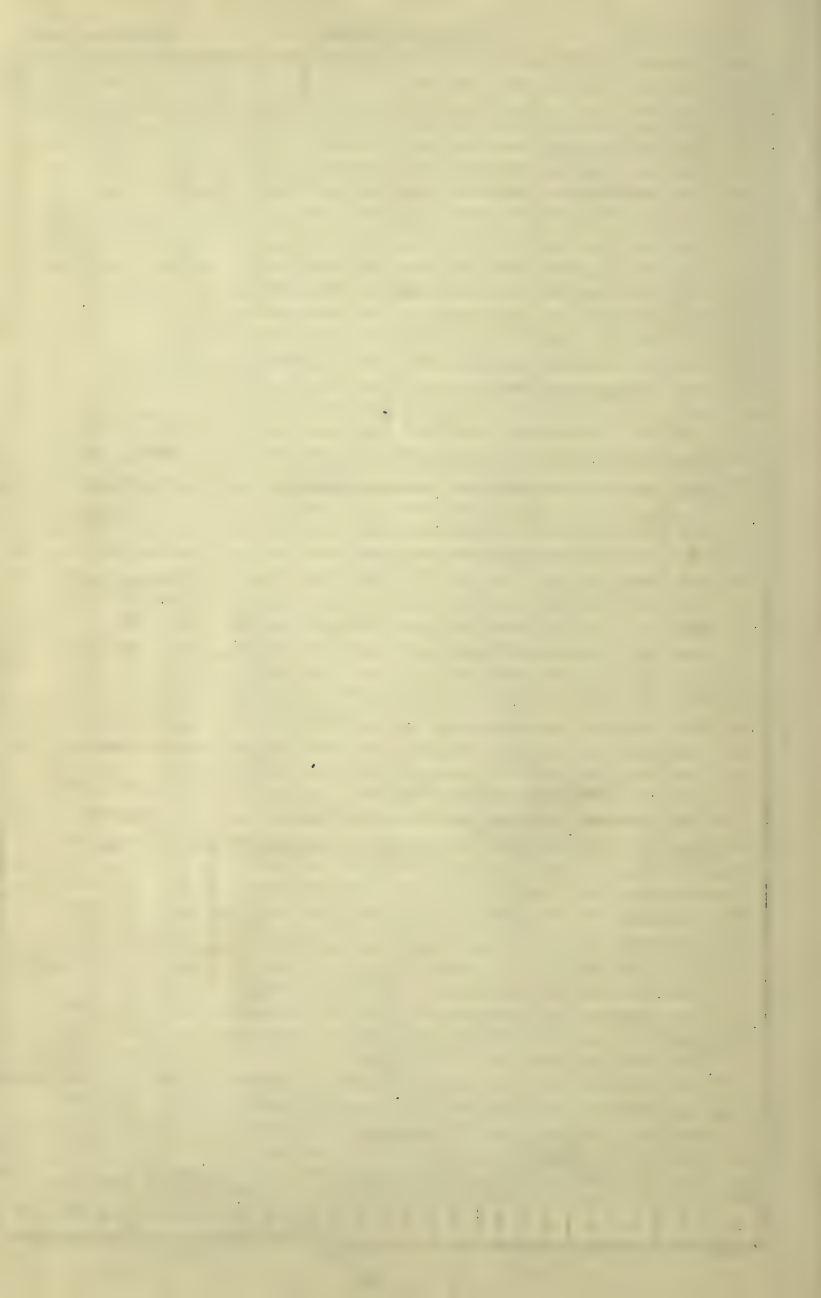
APPARATUS AND SUPPLIES

THE estimate appended has been kindly furnished, at the author's request, by George D. Feidt & Co., 528 Arch Street, Philadelphia.

1. **Apparatus for each student** (cost, $5.95).

Bunsen burner, test-tube brush, retort stand (small, two rings), clamp, deflagrating spoon (small iron), file (triangular), blow-pipe (brass, common), file (round), iron wire gauze, $5'' \times 5''$, tin pan, round, $10'' \times 3''$ high, lead disc for collecting gases, $2\frac{1}{2}''$ diam., 4 lead rings to fit $6 \times \frac{3}{4}''$ test-tube, 100 c.c. evaporating dish, mortar and pestle ($3''$), 2 beakers (straight form, no lip, 100 c.c. capacity), funnel $3''$, gas generating bottle, capac. 250 c.c., with funnel tube and delivery tube, $\frac{1}{2}$ doz. plates of window glass $4'' \times 4''$, 4 salt-mouth bottles 300 c.c. (common, no stoppers), $\frac{1}{2}$ doz. test-tubes $6 \times \frac{3}{4}$, $\frac{1}{4}$ doz. test-tubes 8×1, 1 test-tube, hard glass, $6 \times \frac{1}{2}$, 1 test-tube rack to fit $6 \times \frac{3}{4}$ and 8×1 tubes. Set 4 bottles, 1 liter capacity, enameled or ground-glass labels, for hydrochloric acid, sulphuric acid, nitric acid, and ammonia. Wooden block for holding these bottles, four round depressions in block.

2. **Apparatus to be kept in stock and furnished as occasion requires.**

A. METAL (cost, $9.78, the induction coil being the chief item).—$\frac{1}{2}$ doz. Hoffman screws, lead dish (flat, 75 c.c.), small horseshoe magnet, wire cutter, induction coil $\frac{1}{2}''$ spark).

B. PORCELAIN (cost, $7.20).—Porcelain crucible and cover No. 0, 3 cells (Edison-Lalande or equivalent).

C. GLASS (cost, $16.16).—Beaker (500 c.c.), beaker 1,000 c.c., bulb tube (1″ bulb), burette 50 c.c. grad. in $\frac{1}{10}$ c.c., Hoffman apparatus for electrolysis, lamp chimney (ordinary wide form), U-shaped eudiometer, flask (1,000 c.c.), flask 250 c.c., cylinder graduated 1,000 c.c., Erlemeyer flask 1,000 c.c., separating funnel 100 c.c., retort, capacity 200 c.c. with tubule and glass stopper, U-tube 4″ with side tubes, glass rod, glass tubing. Eudiometer straight (50 c.c. graduated in $\frac{1}{2}$ c.c.).

D. VARIOUS (cost, $7.20).—Corks, wooden (best), corks, rubber, 1 hole, 2 hole, and solid, asbestos board, Christmas-tree candles, filters (common 5″), labels (Dennison's No. 209), magnifying lens, meter stick, yard stick, platinum foil, platinum wire (size for blow-pipe work), copper wire (insulated), iron wire, rubber tubing $\frac{1}{8}$″ internal diam., $\frac{3}{16}$″ internal diam., $\frac{1}{4}$″ internal diam., and large for gas connections.

CHEMICALS (cost, $23.70)

Acid, acetic,
　　" 　hydrochloric,
　　" 　nitric,
　　" 　sulphuric (all of above commercial),
　　" 　hydrochloric,
　　" 　nitric,
　　" 　sulphuric (all of above C. P.),
　　" 　hydrofluoric, commercial,
　　" 　oxalic,
　　" 　tartaric.
Alcohol, 95 per cent,
　　" 　wood spirit.
Aluminium, sheet,
　　　" 　powder, bronze paint,
　　　" 　sulphate.
Ammonium, chloride,
　　　" 　nitrate,
　　　" 　sulphate,
　　　" 　oxalate.

Ammonia water.

Aniline red.

Antimony, metallic,
"   potass. tartrate (tartar emetic).

Arsenic, metallic,
"   trioxide.

Barium chloride,
"   chlorate,
"   peroxide.

Bleaching powder.

Bone-black.

Borax.

Bromine.

Cadmium chloride.

Calcium carbide,
"   carbonate (cracked marble),
"   chloride (crystals),
"   chloride (fused),
"   fluoride powder,
"   oxide (lime),
"   sulphate (plaster of Paris).

Cannel coal.

Carbon disulphide.

Charcoal, lump.

Chrome alum.

Cobalt nitrate.

Cochineal.

Copper, clippings,
"   sheet,
"   wire,
"   carbonate, basic (powder);
"   sulphate.

Cream of tartar.

Ether.

Gold leaf.

Hydrogen peroxide (3 per cent).

Iodine.

Iron (alcoholized).
   Steel wool.

Iron chloride (ferric),
" oxide (caput mortuum),
" oxalate (ferrous),

Iron filings,
  " sulphide.
Kerosene.
Lead (tea lead),
  " granulated,
  " acetate,
  " red lead,
  " dioxide,
  " nitrate,
  " oxide (litharge).
Litmus (cube).
Litmus paper, red and blue.
Magnesium oxide,
     " powder,
     " ribbon.
Manganese dioxide (powder),
     "   " (granulated).
Mercuric chloride,
   " iodide,
   " oxide.
Mercurous nitrate.
Phenol-phthalein.
Potassium (metal),
   " bromide,
   " carbonate,
   " chlorate,
   " chloride,
   " chromate,
   " dichromate,
   " ferricyanide,
   " hydroxide,
   " iodide,
   " permanganate,
   " sulphate,
   " sulphocyanide.
Pyrogallol.
Rosin.
Silver nitrate.
Sodium (metallic),
   " acetate,
   " dicarbonate (baking soda),
   " carbonate (crystals),

Sodium carbonated (dry),
" chlorate,
" chloride (salt),
" hydroxide,
" nitrate,
" nitrite,
" silicate,
" sulphate,
" acid sulphite,
" thiosulphate.
Starch.
Strontium chlorate.
Sugar, grape (glucose).
Sulphur, roll,
" flowers.
Tin, granulated,
" foil,
" bar.
Turmeric paper.
Vaseline.
Water, distilled.
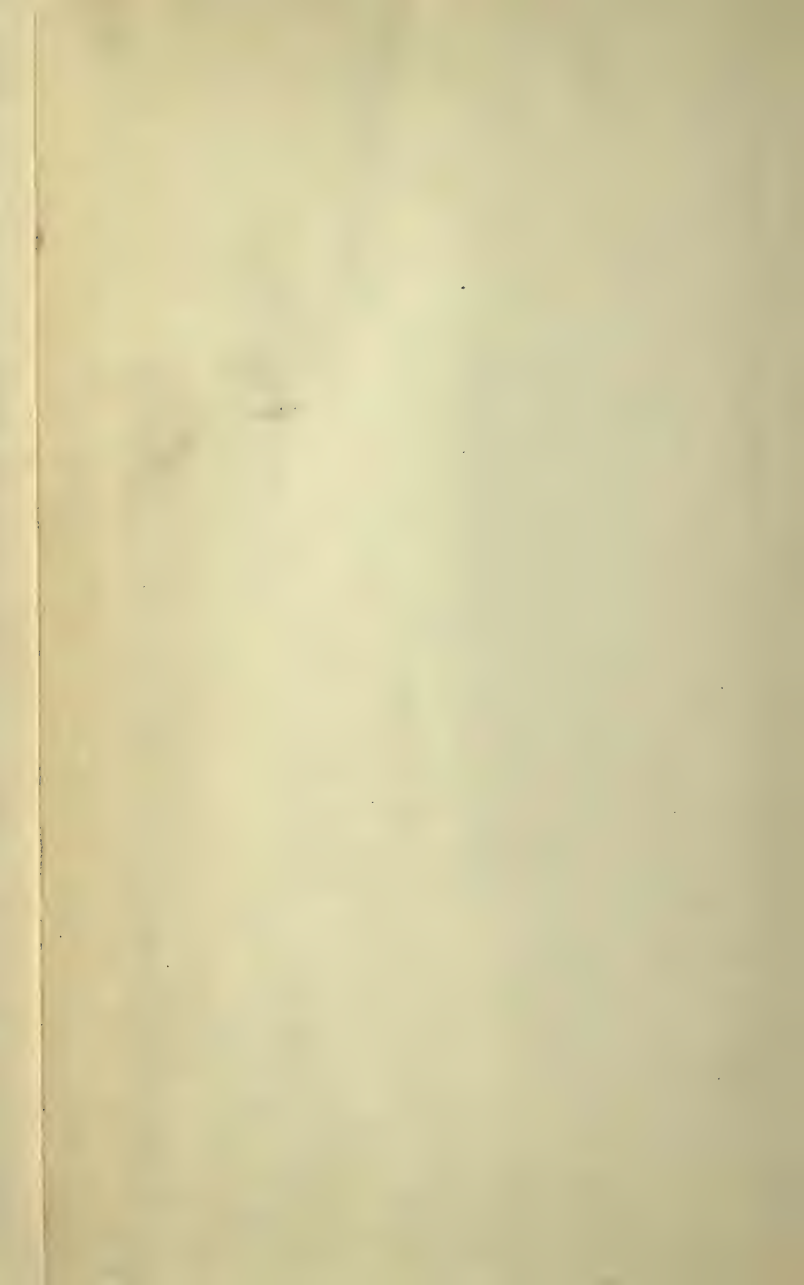Zinc, dust,
" granulated (mossy),
" sheet,
" oxide.

All prices are *net*. The prices of the chemicals are subject to variation. The quantities of the chemicals will be sufficient for a class of six or more to make the experiments.

(5)

14 DAY USE
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LOAN DEPT.

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on the date to which renewed.
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